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ADHESIVES

by

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PREFACE

THIS book was written primarily for the practical man who is interested in adhesives either as producer, consumer, or salesman. It is not intended for the specialist or for those who are concerned with the scientific aspects of adhesives.

No chemical or technical training is required for the full understanding of this book, as the subject is presented from the practical point of view with a minimum of theoretical discussion.

It is hoped that the information given here will be helpful to all those who have always wanted a simple, readable exposition of this subject.

Grateful acknowledgment is made to those who have supplied useful information and who have helped with the proofreading and who prefer to be unmentioned by name. The author will appreciate receiving communications regarding errors or omissions.

FELIX BRAUDE

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ABBREVIATIONS

Bé.	— Baumé (degrees)
C.	— Centigrade (degrees)
cc.	— Cubic Centimeters
g.m.	— Gram
gal.	— Gallon
kg.	— Kilogram
lb.	— Pound Avoirdupois
l.	— Liter
oz.	— Ounce
pt.	— Pint
sp. gr.	— Specific Gravity
vol.	— Volume

INTRODUCTION

THE use of adhesives, i.e., compounds which paste bodies together, started with the first developments of human ingenuity. Saliva, resins, bituminous earth and wax of wild bees gave the first adhesives to man. Prehistoric tribes who, according to their rites, had to bury their dead endowed with foodstuffs, may have believed that the deceased would not worry too much about second-rate pottery and therefore frequently put broken vessels cemented with rosin into the graves. Javelin bone-blades were pasted and bound to shafts and the blades still show remnants of cement.

Later more complex compounds were used. Statues were found in excavated Babylonian temples which had their ivory eyeballs fixed by bituminous cements 6,000 years ago. Adhesives made from white of egg and lime were used by the Goths in decorating small wooden boxes with Roman coins 2,000 years ago. Today the coins still stick firmly to little pieces of rotted oak-wood.

The Romans and Greeks knew veneer and marquetry as well as preservative painting glues. Thus mural paintings were preserved in untouched beauty throughout 2,000 years in buried Pompeii. Common animal glues were mainly used, but some cheese-lime compounds, forerunners of our modern casein glues have been found. The medieval setback in technical culture brought the use of adhesives to a standstill until the period of the Renaissance, which brought a spontaneous development of many new types of adhesives. From this milestone the highway of invention

was never again interrupted and today man disposes of an infinite number of adhesives for the most disparate purposes.

The general conception of an adhesive is that it is a substance applied as an intermediate layer between two surfaces to stick these to each other. This definition, however, is not quite precise as, on the one hand, it does not account for all the substances which can be called adhesives, e.g. it does not embrace paper sizes, the adhesives that bind together fine cellulose fibres to a continuous paper sheet, and on the other hand, it seems to cover metals used to solder together two metal surfaces, which are not ordinarily considered as adhesives.

Adhesives have a great many industrial applications and their requirements vary within wide limits. Pure substances are seldom used as adhesives. In most cases modifying agents are added to the basic adhesive. These modifying agents can be plasticizers, stiffeners, driers and so forth, according to the basic adhesive and the application of the finished product. Colloidal substances owing to their surface properties and viscosity, are more suitable for use as adhesives than crystalline substances. The major part of the adhesives used in industry are colloids.

Adhesives are marketed both in the liquid and solid states. The setting of the adhesive may depend simply on the evaporation of the solvent or may be an oxidation or even polymerization process.

Adhesives can be classified from various viewpoints: e.g. we can differentiate between cold and warm adhesives according to whether the adhesive is used with or without the application of heat; another way of classification would be according to the application field of the adhesive, but in this case the same adhesive would fall under different headings. Here the adhesives will be classified according to their origin.

ADHESIVES OF ANIMAL ORIGIN

1. *Animal glues.*

Animal glues are aqueous extracts from the bones, skins, hoofs or horns of animals. In a hot state this extract is fluid and after cooling it forms a gel which can be dried to a transparent solid. When dissolved in hot water, this gives a fairly good adhesive. Animal glues are widely modified by the addition of various substances and the resulting adhesives may be cold glues, which are preferable for industrial use, or glues which generally speaking have better adhesive qualities and give more uniform and more flexible films than the basic glue.

2. *Fish glues.*

These are obtained from bones and skins of fish. Fish glues are very similar to animal glues and are especially suitable for the manufacture of liquid glues.

3. *Casein adhesives.*

These are precipitated from milk. The precipitate is dried and ground to the required fineness, modifying agents such as alkalis are admixed and with water a paste is formed which is more or less stable. The stability of this product can be extended to months or even years by the addition of suitable stabilizing agents, e.g. nitrobenzene.

ADHESIVES OF VEGETABLE ORIGIN

1. *Gums.*

These are adhesives extracted from trees of the species acacia. Gum arabic is the best known representative of this group. Aqueous solutions of these gums are used as adhesives for various purposes but the quality of the joints

obtained with vegetable gums does not compare favorably with that of the joints formed with animal glues. Vegetable gums can also be modified, especially with plasticizers such as glycerol.

2. *Cellulose adhesives.*

These are adhesives obtained by dissolving cellulose acetate or nitrocellulose in suitable solvents. These are used in the shoe industry instead of rubber base adhesives.

3. *Dextrin-base adhesives.*

These are adhesive substances prepared by the degradation of starch at higher temperatures, by the action of enzymes on starch, or by chemical treatment of the same. Dextrin base adhesives form sticky pastes which are modified by the addition of softeners, plasticizers or driers. These adhesives are used for sticking paper sheets, wooden parts and the like to each other, but the resistance of the joints to moisture is much inferior to that of other adhesives.

4. *Rubber Latex.*

This is the milk sap of the rubber tree, guayale shrub, etc. which shows adhesive properties that are especially enhanced on addition of modifying agents.

5. *Resins.*

Shellac, rosin and other natural resins are also used as adhesives either alone or as additions to other adhesive bases. Alkali resinsates (rosin soaps) are also employed in adhesive mixtures.

SYNTHETIC ADHESIVES

The various synthetic resins such as ureaformaldehyde, phenol-formaldehyde, acrylic, vinyl resins find frequent ap-

plication as adhesives. Their most important use is in the plastic plywoods which are being developed and which seem to be the future material for airplanes, boats and similar devices. In the plastic plywoods the advantageous qualities of synthetic resins are united with those of the wood, so that the resin is more than a mere adhesive in this application; it not only sticks the wood layers together but it gives stiffness, resistance, and durability to the finished product. A plastic plywood cannot only be considered as a wooden mass, the layers of which were pasted together with a plastic, but also as a plastic mass in which wood has been used as a filler.

(The adhesives are applied to surfaces either by hand or by mechanical means. The manual application is mostly done by brushing.) The machines for coating surfaces spread the adhesive with pairs of rollers or with spraying attachments. The adhesive can be applied directly to the surface or a tissue paper can be coated with adhesive and placed between the two surfaces to be stuck together. The adhesion is attained by the application of pressure or both pressure and heat. The adhesive may be applied to either of the surfaces to be joined or to only one. Sometimes a precoating, sealer or preliminary adhesive, is applied and the final adhesive coating is put on after drying the first coating.

There is probably some relation between the chemical nature of the material whose pieces are to be stuck together and that of the adhesive which is most suitable for the purpose. However, no accepted theory has been developed in this respect. The only rule which seems to hold for many, but not for all cases, is that polar adhesives are suitable for pasting together polar materials, whereas they are not suitable for use with non-polar materials. The case is similar with the use of non-polar adhesives and non-polar materials.

As to the forces that give rise to adhesion between adhesives and adherends the theory differentiates between two kinds of adhesions: mechanical adhesion and specific adhesion. The first is the adhesion observed between porous surfaces in which the adhesive keys the parts together. Specific adhesion is observed between smooth surfaces which are held together by forces similar to the molecular forces which give rise to cohesion, holding together the particles of a material. Of course, there is always a combination of these two kinds of adhesion and in most cases one of them is predominant.

Formulas for adhesives will be found throughout the book, each one illustrating a particular type. Details of procedure are of the utmost importance in obtaining satisfactory results, but unfortunately some of these details cannot be described successfully on paper. It is best to repeat the formula accurately several times, making minor changes in technique each time. If difficulties are still encountered, it is wise to obtain the assistance of a qualified expert.

CHAPTER I

THEORY AND APPLICATION

MANY explanations for the sticking power of adhesives have been advanced, but even today, the chemist and physicist are unable to give a completely satisfactory explanation. Adhesion is probably brought about in several ways. The first adhesives were gelatinous and, for a time, the false conclusion was drawn that only gelatinous solutions could be adhesives. According to one theory, the adhesive fills the interstices and interlocks the surfaces that are glued. This explains why rough surfaces are easier to glue than smooth surfaces in some cases, but it fails to explain the perfect results obtained in laminated glass.

Adhesion is now theoretically explained on a basis of molecular attraction and repulsion. McBain and Lee found that strong joints can be made with any material which can wet both surfaces and solidify in place. They made excellent joints with sulphur, oleic acid, and many other chemicals. To understand the problems in principle, one has to consider two different forces acting between pasted bodies, e.g., two boards glued together.

1. *Force of adhesion* working between the molecules of the adhesive (glue) and the pasted surface (board). This force tries to join adhesive and surface. It wets the wood with glue, and opposes the separation of these two layers. Wetting is regulated by the internal force called surface tension, which tries to diminish the surface as much as possible and causes the round shape of a drop. In order to wet the surface at all, the surface tension of the liquid must be less than that of the surface to be wetted (water

wets wood but not fat). The more diffused these layers are the more adhesion will have to be overcome before the joint separates. Summary: Rough ("hills") or porous ("canyons") surfaces therefore will, under same circumstances, exert more adhesion than smooth or polished ones. Adding of compounds which diminish the surface-tension (e.g. soap) promotes adhesion.

2. *Force of cohesion* (tensile strength) working within the adhesive. Water adheres perfectly to wood, but it does not have enough cohesion to overcome the slightest pull. Below zero it would become a temporary adhesive in the form of ice.

Note: Sometimes the inner molecular structure of an adhesive is not favorable to adhesion because the great molecules (smallest free parts) cause too much inner friction and therefore too little wetting. By appropriate means (boiling, adding of chemicals, etc.) a breakdown of these aggregated elementary parts is forced. After passing a narrow bracket, an adverse effect becomes evident. The better adhesion is overwhelmed by a weakened cohesion, and the transformed adhesive becomes mechanically inferior.

Other ways of increasing adhesion or cohesion of an adhesive:

- a. Adding the effect of air pressure (glass plates).
- b. Mixing in special ingredients (sodium silicate).
- c. Using it at a specially favorable temperature (warming to prevent glue from becoming too viscous or non-wetting).
- d. Adding pressure.
- e. Altering the surfaces.

The surfaces to be joined, should be clean, free of rust, dirt, or oil. The adhesive should be applied in a thin uniform film. In some cases, it is best to let the adhesive dry

somewhat before applying pressure to the surfaces. When working with porous surfaces, a thin coat of adhesive, enough to fill the pores, should be applied first. This is allowed to dry before a second, heavier coat, with which the joint is made, is applied.

Adhesives may be applied in widely different ways, each of which offers its own specific problems. The simplest method, brushing it on, requires a minimum of equipment. In this case, the adhesive must be spread well into a uniform film and if large surfaces are to be covered, it must not set too rapidly.

In the glazing method, the adhesive is spread on a zinc sheet and the paper to be glued is placed on this. When the paste is partially set the paper is removed.

The dry method is applicable to adhesives that are thermoplastic (soften on application of both heat and pressure). In this case, the adhesive is spread on the surfaces to be glued. It is then dried and the joint is made by placing the surfaces (as two pieces of wood) in a heated press. This method is used in the manufacture of plywood.

In the gumming machine, the adhesive is spread on paper, textiles and similar materials by means of rotating cylinders.

The modern, completely automatic machine has presented difficult problems to the adhesive manufacturer. The speed with which these machines operate has increased from year to year, and with each increase, improvements had to be made in the adhesives. For use in these machines, it is necessary that the adhesive have high initial tack as well as the ability to set very rapidly.

CHAPTER II

TESTS FOR ADHESIVES

SIMPLE, routine tests on adhesives are useful in determining their quality. More accurate evaluation requires the services of a chemist and chemical laboratory. The scientific methods of chemical and physical testing are complex and fall outside the scope of this book. More detailed information is available in Allen's "Commercial Organic Analysis".

In color, the adhesive should be no darker than other representatives of its class. Dark color, in many cases, indicates inferior raw materials or poor workmanship, decomposition, or fermentation.

The odor should not be strong or objectionable. A bad odor probably indicates fermentation. A strong odor of perfume or nitrobenzene arouses the suspicion that it was added to hide an obnoxious odor.

The viscosity, which in many, but not in all cases, is proportional to adhesion, may be judged roughly by stirring with a rod. A better way is to measure it in one of the many viscometers on the market. In making this test, one should keep in mind that the viscosity of an adhesive may change a great deal shortly after it is manufactured. The glue should stand at least over night to reach equilibrium before it is tested.

The alkalinity may be determined by diluting the adhesive with a little water and testing it with blue and red litmus paper. If the red paper is turned blue, the adhesive is alkaline; if the blue paper is turned red, the adhesive

is acid; and if they both remain unchanged the adhesive is substantially neutral. A somewhat better way is to make this test with a solution of phenolphthalein which is prepared by dissolving 1 gram phenolphthalein powder in 500 cc. alcohol. For the test, 5 grams of the adhesive are mixed with 20 cc. water and 5 drops of the phenolphthalein solution are added. If the solution turns deep red, the adhesive is alkaline; if slightly pink, the glue is slightly alkaline and if the solution remains colorless, the adhesive is either neutral or acid.

The practical test is the most important one of all. In this, the adhesive is tested under the conditions in which it is to be used, sometimes alongside of a standard material. The joints may be tested for strength and other pertinent tests may be made. According to the many conditions which determine the practical use of an adhesive, this kind of test may also be accomplished in various ways. The joint is subjected to mechanical vibrations, bending, pulling, shearing, etc. The atmospheric influences of heat combined with moisture are studied by "cabinet" methods. The joint is exposed in a chamber of observation, sometimes for months, to incessant changes of temperature and humidity. This, of course, may be combined with chemical influences (addition of aggressive gases, or fluid agents, etc.) in order to duplicate the conditions which the adhesive may have to withstand later in its practical application.

Glues for wood are given special tests. For example, two pieces of wood are joined by glue. After drying, a force is applied at right angles to the joint. If a clean break occurs the glue is rejected. If the wood is splintered at the same time, the glue is of satisfactory quality. For accurate tests, a dynamometer is used. This is a device which measures accurately the force required to pull two glued surfaces apart.

Dulac¹ suggests the formation of films of adhesive on glass. After drying, the films can be compared by scratching and scraping. The tests comprise observation of crystallization, evaporation of the solvent, strength of the tack by pasting on pieces of paper, resistance to humidity by dipping such papers in water, etc.

In cases of strong glues, some of the glass chips off when the adhesive film is scraped. The film must show no signs of crystallization as that weakens the adhesion.

The flexibility and plasticity of an adhesive can be determined by forming the films on a surface to which the adhesive will not adhere, such as a Bakelite or a Celluloid sheet or an oiled glass. After drying, the films of dry adhesive are peeled off and examined for toughness, elasticity and flexibility. This film-testing has only *indirect* bearing on the practical usefulness of the adhesive and does not allow too far-reaching conclusions.

There are many other simple methods, such as loading little rods (cylinders) made from the adhesive or some material soaked with the adhesive, with mounting weights of mercury until they break, and so forth, but in view of so many complicated and interdependent influences only a test will give valuable results which imitates the strain to be expected.

¹ Dulac, R. and Rosenbaum, J. L., *Industrial Cold Adhesives*, Charles Griffen & Co., Ltd., London (1937) p. 22.

CHAPTER III

RAW MATERIALS

FLOUR

CEREAL flour consists of two principal components which are of interest to us. The greater portion is a carbohydrate which we know as starch and a lesser portion is a protein material called gluten. In rye flour there is 60 per cent starch and 10–11 per cent gluten; in wheat flour there is 65 per cent starch and 12–15 per cent gluten. Flour pastes depend largely on their gluten content for their adhesive properties although the starch is also a factor. The gluten content of wheat flour varies with the country in which it was grown, and other complex factors. Wheat is the only grain which can be used widely for adhesives for its gluten content.

Analysis of gluten in flour. Work 30 grams of flour with 12–15 cc. of water into a stiff dough. Allow to stand for 1 hour. Wash in running water until all the starch has been washed out (until the water that runs off the dough is absolutely clear). Leave the dough under water for another hour. Wipe the wet paste with a cloth to remove the excess water, and weigh. Dry the dough at 98°C. for 40 hours and weigh again. This weight is the yield of dry gluten.

The gluten dough before drying should be plastic, ductile and malleable as well as elastic. It can be drawn out into threads easily. If it does not stretch easily and cling together it is of inferior quality. It should be light yellow in color. A dirty gray color is another indication of an inferior grade.

Flour may be purchased in bags or barrels and should be stored in a dry place protected from vermin and rodents. In its chemical analysis, it is tested for moisture, ash, gluten, starch and acidity. Under the microscope, it is examined for foreign material, starch granules, fibres, and the like. There are other practical tests, such as specific weight, smell, taste, touch, color, yield of dough (100 parts rye should give 150 parts dough) and above all, baking-ability. The last property, until recently, could not be linked with any theoretical test.

STARCH

Starches are found widely distributed in nature. They are formed by the green parts of the plant from the carbonic acid of the air and water and are stored as reserve food in roots and tubers. They may be separated in commercial quantities from many different plants such as wheat, corn, barley, tapioca, cassava, rice, potato, sweet potato, and many others. The properties of these starches differ widely, depending not only on their source but also on the process of manufacture.)

The following brief description of the process of separation of starch from potatoes is an example of the methods used for extraction of this valuable raw material from its sources.

The potatoes are warmed in water for a few hours to loosen the clay and loam. They are then washed thoroughly. Next they are fed into a rasping machine which transforms them into a pulp. The cells containing the starch are ruptured in this operation and the more thoroughly this step is carried out, the better the yield of starch. The yield may be improved by grinding the pulp in a ball mill. The pulp consists of a mixture of fibres and starch granules, which are separated by fine sieves. The starch

is then further purified by settling in water. Finally, the starch granules are separated from the liquor in a centrifuge and dried.

Starch, whatever its source, is generally sold in the form of lumps. It is a white tasteless powder which is insoluble in water and all other known solvents. Some physical or chemical changes occur as soon as an attempt is made to bring it into solution.

Starch granules consist of two parts, the enveloping sphere containing complicated phosphorous compounds (60–80%) and the central liquid (40–20%). Only the enveloping spheres yield derivatives with adhesive properties.

Starch has been found to be a system of interchained sugar (glucose) molecules, which will break down into smaller groups (such as dextrans, syrups, or glucose-sugar) upon the application of heat, chemical agents or enzyme action (fermentation).

Starch is hygroscopic, a dry starch contains about 20 per cent moisture. Even in vacuum it contains 10 per cent moisture. It is sold in cartons, bags and barrels and should be stored in a dry place protected from vermin or rodents.

The simplest test for starch is the characteristic blue color which is developed when starch or its solution is treated with a drop of iodine solution. The solution of iodine is prepared by dissolving 0.5 gm. iodine and 1.5 gm. potassium iodide in 25 cc. distilled water.

Amazingly different results are obtained with the different starches derived from numerous natural sources. For this reason, it is very important for the consumer to identify the type of starch he is buying. Unfortunately, this is not a simple matter, considerable skill and experience being required. Starches are best identified by inspection under the microscope and by their appearance when examined in polarized light. As has been stated previously starch

occurs in the form of granules. The size and shape of these granules under the microscope is characteristically different for each type of starch. The diameter of these granules is not constant even for any one type but in the following table the maximum diameters in millimeters are given for a number of common starches. These dimensions are only approximate. Investigators differ in their reports.

TABLE 1

<i>Starch</i>	<i>Maximum diameter in millimeters</i>
Arrowroot	0.014
Potato	0.014
Sago	0.070
Wheat	0.028
Corn	0.030
Tapioca	0.028
Rice	0.022

In addition to the differences in size and shape, characteristic markings are seen on the starch granules when observed under the microscope. Starch granules also give characteristic patterns when examined in polarized light. A detailed discussion of this subject is found in Allen's "Commercial Organic Analysis", Volume 1, page 515-524.

For the small consumer, the best test is to prepare an adhesive with the sample in question to see whether it gives the desired result. This test is necessary in any case. The integrity of the source of supply must be depended upon. When starch is heated in water to a certain temperature, the starch granules swell, burst and finally produce a viscous pasty liquid. This occurs gradually, as some granules burst more rapidly than others. The temperature at which complete gelatinization occurs for a number of common starches is given in the following table. Pure

starches gelatinize more readily than impure products. For crude materials, the temperature of gelatinization is much higher than those given in the table.

TABLE 2

<i>Starch</i>	<i>Temperature of complete gelatinization</i>
Potato	65° C.
Corn	75° C.
Barley	80° C.
Wheat	80° C.
Rye	80° C.
Rice	80° C.

Treating starch with dilute acids makes it soluble in water without profound change in chemical composition. The product thus obtained has lost its paste-forming quality and is known as soluble starch. It dissolves in hot water and gives a blue color with iodine. Root starches produce objectionable odors.

When alkali is added to a starch solution, the opalescent liquid becomes transparent due to the dissolving of the starch cellulose. When the alkali is neutralized, it does not revert to its original condition because the chemical has produced a permanent change in the starch. (A starch solution formed by boiling starch in water has very little sticking power, but when alkali or certain other chemicals are added, the solution develops strong adhesive properties, which are retained even if neutralized.)

DEXTRINS

The complex starch molecule can be broken down completely to glucose under carefully controlled conditions

and numerous, valuable, intermediate products may be obtained. These simpler carbohydrates are called dextrins, but their exact nature is not as yet definitely known. So many different properties can be developed by these changes that the basis for hundreds of different adhesives for as many different applications is formed. For many purposes, dextrins are better adhesives than the starches from which they were derived.

In contrast to starch most of the dextrins are soluble in cold water and do not give a blue color with iodine.

A special type of dextrin made primarily from maize starch is known as British Gum. Solutions of British Gum are more viscous than those of dextrin, probably because some of the starch remains unchanged.

The starches most frequently converted into dextrin are those derived from corn, potato, and cassava. Wheat and rice are somewhat more difficult to dextrinate but are preferable in some cases.

In the first step, called "maturing", the starch is left to stand in contact with the acidulated water for a period ranging from twelve hours to five days. The more completely the acid penetrates the starch granules, the more readily the transformation to dextrin occurs and therefore the lighter the color of the final product. After maturing, the starch is dried and then roasted. When cool, the dextrin is moistened again and ground.

Sulfuric acid or phosphoric acid may also be used as catalysts, but in these cases the process must be carefully controlled.

It is reported that spraying the hot dextrin with 3-5% formaldehyde after the acid treatment gives a more soluble product whose viscosity and color is unchanged by this treatment. Starch may be sensitized to roasting by treatment with hypochlorite solution.

Dextrin is infrequently produced by enzymatic processes,

which are of no outstanding importance. The fermentation caused by malt added to a cold starch solution is used by manufacturers of finished brands of dextrin adhesives.

We have already seen that dextrin is not a pure chemical substance but a mixture of complicated products which are practically impossible to define at present. However, dextrans may be grouped in several classes, each of which have certain dominating characteristics. Chemically, dextrans are classified in three groups:

1. Amlodextrans which give a blue color with iodine solution and are soluble in 25 per cent alcohol.
2. Erythroextrans which give a reddish brown color with iodine solution and are soluble in 55 per cent alcohol.
3. Achroextrans which give no color with iodine solution and are soluble in 70 per cent alcohol.

In addition, dextrans are characterized by two chemical tests, cupric reducing power and optical rotation.

From a practical consumer's point of view, dextrans fall into three groups also:

1. White dextrans which are soluble in cold water to the extent of 20-75 per cent.
2. Slightly colored dextrans which are about 97 per cent soluble in cold water.
3. More highly colored dextrans which are almost completely soluble in cold water.

The progress of the formation of dextrin in the roasting process can be controlled by the following simple test:

Add 20 gm. of the dextrin sample to 200 cc. water in a 500 cc. flask. Shake five minutes and filter the solution through a pleated filter paper. Determine the density of the filtrate with a Brix hydrometer. The reading multiplied by ten gives the per cent dextrin soluble in cold water.

Dextrin manufacture is something of an art besides being a science. The rate of conversion varies with the size of

the starch granule. Large granules are dextrinated more rapidly than small granules, therefore it is advisable to examine a starch sample under a microscope before fixing the length of time for roasting.

Corn starch dextrins have a distinctive odor and flavor and are, as a rule, used for cheap work except when used in combination with potato or cassava dextrins to impart certain desirable properties. Potato and cassava dextrins are generally used for high grade work. For adhesive stamps, labels and envelope flaps, cassava dextrin is preferred because it is tasteless (potato dextrin is bitter) and is a somewhat stronger adhesive.

In the roasting process, more or less sugar (glucose) is always formed. Too much glucose is objectionable because it makes the dextrin hygroscopic.

The properties desired in a dextrin besides strong adhesiveness are high solubility, little or no color, high viscosity or body in solution, and no taste or odor. No one dextrin meets all these requirements because, as a rule, a very soluble product gives a solution of low viscosity and impaired adhesion. One other property should be checked. Some dextrin adhesives tend to revert causing the solution to lose its viscosity on storage and become cloudy and pasty. This is most noticeable in highly concentrated solutions and with only partially converted dextrins. It is reported that dextrins that are difficult to form, such as those prepared from small starch granules, revert most. If sold in solution, a dextrin adhesive should be stored for at least one month and should be filtered before shipment. Low temperatures increase the tendency to revert.

Commercial dextrins are amorphous, white or yellow powders which are deliquescent (become pasty in the presence of moisture) and non-volatile. For practical purposes, they are best tested by preparing a trial lot of ad-

hesive. In the chemical laboratory, they are analyzed for ash, acidity, insoluble matter in hot and cold water, starch, and above all the grade of break-down is calculated by determining the percentage of glucose present by use of a polarimeter.

Dextrins are sold in fibre drums, bags and barrels. They should be stored in a dry place protected from vermin and rodents.

CASEIN

Casein is a valuable raw material for adhesives where greater water resistance is required than can be obtained with starch or dextrin adhesives. It is the protein found in milk and is obtained by coagulating skimmed milk. Cow's milk contains 2.00–4.5% casein; other milks differ widely in this respect. Casein is probably not one protein but a mixture of different proteins whose properties depend upon the process of manufacture. It is for this reason, probably, that authorities differ on the characteristics of casein products.

Casein is separated from skimmed milk in three ways. The most common process is to coagulate the milk with dilute hydrochloric or sulphuric acid. A second procedure is to let the milk sour by itself or by the addition of the bacterial culture which produces coagulating lactic acid. Finally, the protein can be coagulated by the addition of an enzyme called rennet found in calf's stomach. The amorphous, white precipitate obtained by these methods is washed, filtered, pressed out, washed with warm water (3 times), filtered and pressed again, disintegrated and dried.

Casein manufactured by the first process is known as acid casein; by the second process as lactic casein and by

the third process as rennet casein. Acid and lactic casein resemble each other but rennet casein differs from them in certain properties.

Rennet casein is generally sold in lump form and is white in color. Acid casein is sold either in powder or lump form and is pale yellow in color. The two types differ on chemical analysis. Rennet casein has eight times as much ash as acid casein.

If rennet casein is washed carefully, with dilute acid, the ash may be reduced and the resulting product behaves very much like acid or lactic casein. High ash increases the viscosity of the glue and reduces the time during which it is workable. Rennet casein, low in ash, is as soluble in borax, sodium carbonate or bicarbonate and trisodium phosphate as acid or lactic casein.

Casein solutions are viscous, viscosity depending upon the type of casein, the manufacturing process, the alkalinity of the solution and its age. Acid casein finds wider application in adhesives than rennet casein because of its better solubility.

Casein, a hornlike transparent mass, swells in water, but dissolves only after adding alkali. After standing for some time in water it becomes far more water-soluble. Ammonia, borax and sodium carbonate are widely used to bring casein into a real solution.

Casein is precipitated from solution by acids, heavy alkalis and metal salts. Formaldehyde transforms it to a plastic (Galalith). The first stages of this transformation show increased stiffness of the casein involved. This phenomenon (to harden and insolubilize casein layers) is used to obtain special paper and textile sizes.

Casein above all is the base of an important group of adhesives distinguished by their water-resistance and therefore used by the woodworking industries (plywood, veneer, etc.). Only recently it has had to yield ground to the ad-

hesives based on artificial resins, which excel still more in water-resistance and are bacteria-proof.

More details about the chemistry of casein adhesives are found in Chapter VI.

Casein is available in huge quantities and for years has been the object of constant research. In recent years, many new products of interest to the adhesive industry have been developed.

"PROTOVAC"

A new series of casein derivatives under the trade name of "Protovac" has been placed on the market. The "Protovacs" are casein derivatives which are modified both in a physical and chemical way by treatment with heat and pressure and by reaction with a number of chemicals such as borax, ammonium hydroxide, caustic soda, triethanolamine, alkaline earth hydroxides and many others. These new products have many applications but we shall consider only those that are of importance in adhesives.

"Protovac 20" is a sodium caseinate, soluble in water without the addition of alkaline reagents. It is light in color and soluble in hot and cold water. The water solution is neutral and must be protected by a preservative in order to prevent putrefaction. The solution gels if appreciable amounts of formaldehyde are added.

"Protovac 8397" is a caseinate which is soluble in hot water without the addition of alkaline reagents. It gives a thin solution in water which is light in color, practically neutral and stable in viscosity. When formaldehyde is added to these solutions, they will remain stable for months if properly prepared.

If long stability in the presence of formaldehyde is not required "Protovac 8745 may prove useful. This product is soluble in hot water, light in color and faintly acid in

reaction. The viscosity of the solution is medium but tends to become thinner on standing. Formaldehyde causes the solution to gel after twelve hours.

Two compounds, Plasticizer 11 and Plasticizer 22, are made for addition to the Protovacs to make them more flexible. Plasticizer 11 is lighter in color than Plasticizer 22, but the latter is less expensive.

Being a protein, casein must be protected from bacterial decomposition. It should be stored in a cold, dry place protected from vermin. This applies to the modified proteins and the Protovacs as well. Casein and its derivatives are sold in sacks, fibre drums and barrels.

SPECIFICATIONS FOR CASEIN

The following simple specifications should be established for acid casein:

The casein should contain no more than 10–12 per cent moisture and should be free of impurities. The powder should be light to butter yellow in color and the odor should be weakly milky. A strongly acid, rancid, cheese-like odor indicates decomposition. The taste should be mild, not strongly acid.

The odor can be best determined by shaking a sample of the casein in hot water.

Solubility in borax is an important property and the acid casein should pass the following test:

Stir 15 g., coarse casein in 60 cc. water and let it stand for at least two hours to swell.

While stirring vigorously, add a solution of 2.3 g. borax in 15 cc. water. Heat to 50°C. on a water bath while stirring continuously. The casein should swell gradually and finally go almost completely into solution. Impure casein does not dissolve completely and forms large lumps. On cooling, the solution should be viscous, free of suspended

solids and smell faintly milky. A streak of this solution on glass should show practically no undissolved glassy particles.

Chemical analysis should show that the casein contains little fat and no more than 5 per cent ash (rennet-casein, 7-8.5 per cent).

Pure casein derivatives are generally too brittle to be good adhesives by themselves.

VEGETABLE GUMS

Historically, gum arabic is one of the oldest of adhesive compounds known to man. During the past few decades, its use has gradually fallen off because of the development of dextrans which replace the natural product.

Gum arabic is the dried exudation from various species of African acacia. The highest grade is sold in the form of colorless lumps of varying sizes, full of minute cracks. A similar gum, but of lower quality, is sold under the name of Gum Senegal. This comes in reddish or yellowish lumps about the size of a pigeon's egg. It is less readily soluble than gum arabic and its solution becomes very dark in color on standing. Gum arabic has a very faint odor and a mucilaginous taste.

There are many grades of gum arabic on the market. The most expensive are practically colorless, give the most viscous solutions, and are free of dirt and foreign matter. The low grades may be adulterated with plum or cherry tree gum, starch or dextrin. A good grade should dissolve almost without residue in cold water and should not contain more than 4 per cent ash. It should not give a blue color with iodine, which would indicate adulteration with starch, or a red color with Fehling's solution which would indicate adulteration with dextrin.

Gum tragacanth is the dried gummy exudation from

certain species of astragalus. It is sold in the form of ribbons, powder or flattened, horny masses. The gum is hard, tough, odorless and tasteless. A good grade is practically colorless and free from adhering dirt, wood or foreign fibres. The better grades give solutions of higher viscosity than the others. Gum tragacanth swells in water rather than dissolves. It is used to increase the viscosity of a solution, i.e., to thicken it, although it has no adhesive quality. Gum karaya is similar to gum tragacanth but gives stringier solutions than the former.

Gum arabic, senegal, tragacanth and karaya are sold in bags and boxes and should be stored in a dry place. Gums from cherry, plum and peach trees find minor applications as adhesives.

GLUES OF ANIMAL ORIGIN

Animal glues were probably first observed when prehistoric men boiled special parts of game or fish and found a gel left in the pot. Glues have been used since the earliest times. Pliny refers to glues, mixed with gums, milk, eggs, and wax, as paints used by the ancient Egyptians.

Animal glues are derivatives of 3 proteinic compounds:

1. Collagen: found in skins, scales, isinglass.
2. Ossein: found in animal bones, horn pith.
3. Chondrin: found in animal cartilages (larynx, etc.).

Note: 3 is of no practical value. Cartilages are always separated from 1 and 2.

Collagen and ossein are nearly identical compounds. The former is obtained from (1) tendons and the corium layer of skin (scrap from the butcher or tanner); (2) trimmings obtained after passing hides through the fleshing machine, which removes all the adhering flesh, and tissue, by extracting with lime water or dilute alkali and thoroughly wash-

ing with water. This corium, or "true skin" is for the most part composed of tender fibres, the "white connective tissue," which is the main source of collagen and derived glues.

Ossein is prepared by extracting degreased bones (after removing marrow) with dilute hydrochloric acid to remove the hard inorganic "skeleton". 40 per cent of the dried bone is inorganic hard substance (calcium carbonate and tricalcium phosphate, a highly important fertilizer); 60 per cent is organic material, mainly ossein.

Collagen is converted into leather by tannic compounds, by heating it in water for several hours at 80–90°C. until it is converted into *gelatin*.

Gelatin is a well defined chemical compound; but the trade uses the name "gelatin" in reference to glues of better quality or higher purity. The same gelatin results from ossein.

Properties of gelatin:

1. Immersed in cold water it swells to many times its normal volume and the swollen jelly goes into solution readily at about 35°C.
2. The viscosity varies greatly with slight alterations in temperature, concentration, additions, etc.; therefore, viscosity is a sharp indicator for gelatin.
3. Solutions of one or more per cent of gelatin, allowed to stand at about 10°C. form a firm jelly, but mixed with acetic or nitric acid gelatin loses this quality.
4. It lowers the solubility of easily soluble salts and increases solubility of slightly soluble salts.
5. It is insoluble in ether, chloroform, carbon disulfide, benzene, absolute alcohol or 10 per cent alcohol at freezing point.
6. Tannic acid precipitates gelatin quantitatively.
7. Potassium dichromate reacts with gelatin in the pres-

ence of light to produce a jelly, which on drying out is insoluble (used for silkscreen stencils and printing processes).

8. Formaldehyde produces, with gelatin, a condensation product rendering the latter insoluble.
9. Gelatin is inclined to rapid bacterial decomposition.
10. Its solutions are strong adhesives.
11. Heated with or without mineral acids or alkalis, gelatin rapidly breaks down to simpler proteins and compounds.

Important: The more gelatin is kept undisturbed the more its valuable properties, especially its sticking power will be preserved. This means: a. beware of bacterial decomposition of the raw materials as well as the finished products during production, storing, shipping, and using. b. beware of chemical and physical decomposition by applying short and gentle processes. The many details in glue-manufacturing are based upon these two points.

Manufacturing of Animal Glues:

1. *Hide glue:* Appropriate hide parts, obtained from the butcher or tanner, are washed and then subjected to the liming process. The stock is thrown into concrete vats containing fresh milk of lime. The time of the soak (milk of lime frequently changed) depends principally on thickness and kind of stock and varies from 30–60 days, until swelling and transparency result.

Alkali, hairs, etc. are then removed. This is done in tumbling barrels, or cone mills until the wash water runs clear and nearly neutral. By gentle indirect vapor-heating, the lime-prepared gelatin is extracted and solved. The type of glue varies with the number of wash water used.

The glue solutions are cleared from lime soaps, fat

compounds and other impurities by adding pulp and filtering. The last "clouds" are taken away by precipitating voluminous calcium phosphates or coagulation (by heating) of egg albumin. These aggregates will collect and hold, by adsorption, the objectionable substances. The liquors are now sent to the vacuum pans which use very low pressure steam and maximal vacuum to shorten the time of evaporation and to keep down thermal and bacterial aggression.

Antiseptics, bleaching compounds, pigments are added (if "white glue" is desired). The concentrated liquor is run into cooling pans, cut and dried on frames in drying alleys.

2. *Bone glue*: Bones are washed, and then degreased by benzene or gasoline extraction. The organic portion of the matrix (ossein) is gained and transformed to gelatin by:
 - a. prolonged treatment with dilute acid which removes all inorganic hard matter. The remaining ossein can be limed and treated like hide-collagen. The solved calcium phosphates are precipitated and give high-grade cattle-food;
 - b. treating the degreased bones in autoclaves (pressure tanks) by alternate application of steam pressure and water, passing the tanks in counter current (fresh water on the most exhausted bones). The remaining, soft, inorganic part is used for various types of fertilizers, "super-phosphates", etc. The glue solutions are treated in a manner similar to that used for hide glue.
3. *Glues of marine origin*:
 - a. *Isinglass*: The swimming bladders of sturgeon and other fish are cleaned, dried and shipped. On soaking in cold water isinglass, which represents *pure collagen*, swells slowly. It becomes gelatin and

gives solutions only after heating. It is frequently adulterated and, because of its high price, is used only as clarifying agent for the better beverages, ingredient for few types of cements, and in silk sizing.

- b. *Liquid fish glue*: Heads, waste and skins from the dried salted "ground" fish (cod, haddock, etc.) are boiled and treated like hides. The resulting fish glues remain liquid and need preservatives. They are widely applied as strong ready-to-use adhesives in spite of their characteristic odor.

To improve the proportion between surface and volume, i.e., to shorten the time of swelling during which bacterial decomposition may be initiated, glues are manufactured in forms other than the old-fashioned cuts, showing the impress of the frame nettings:

- a. *Films*: Spread by vacuum dryers over internally heated drums.
- b. *Powder*: Obtained by desintegrating dried glue, or by atomization of the liquor into a rapidly moving current of hot air.
- c. *Pearls*: (most important of all) Formed by dropping concentrated glue-solutions into a cooling agent, e. g., heavier gasoline.

Glue blocks need about 24 hours swelling-time, pearls only about 1-2 hours.

SODIUM SILICATE

Sodium silicate is an adhesive that is entirely inorganic or mineral in composition. It is manufactured by the fusion of sand and caustic soda and gives colorless viscous solutions with water. Generally it is sold as a concentrated solution with some water present, but it may also be obtained in a dry, powdered form. Its composition varies,

depending upon the ratio of sand and caustic soda used in the fusion and the properties vary accordingly. Sodium silicate is valued as an adhesive because of its excellent glueing properties, low cost and rapid drying. Its chief shortcoming is its strong alkaline reaction. It frequently is used mixed with other adhesives.

Sodium silicate is sold in metal cans and drums. It is perfectly stable and may be stored indefinitely.

ALBUMINS

Dry egg albumin, the dried whites of egg, finds application in some special cases. It is a colorless adhesive but its high cost limits its use.

Blood albumin is obtained by drying clear blood serum after removal of the blood corpuscles, by centrifuging.

METHYL CELLULOSE

Methyl cellulose is a chemical derivative of cotton, or a pure cellulose derived from wood. It is a relatively new product and is sold in several grades based on the viscosity of the solutions they produce.

Methyl cellulose is a colorless, tasteless, odorless substance that looks like compressed cotton. It is more soluble in cold than in hot water and produces colorless solutions of varying viscosities. It is an excellent thickening agent but because of its recent development all its possibilities in adhesives have not as yet been established.

‡ Methyl cellulose is stable in the presence of acids and alkalis and is not subject to bacterial decomposition. Allied to methyl cellulose is ethyl cellulose. To the same group belong practically, although not chemically, compounds of cellulose and acetic acid or nitric acid (acetyl- and nitro-

cellulose respectively). This subject is treated later under adhesives insoluble in water.

ALGINATES

The alginates are obtained from a class of marine plants called algae, especially the Laminaria. The sodium salts are soluble in water and act as thickening agents. They vary in color from practically white to light brown.

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CHAPTER IV

FLOUR PASTES AND STARCH ADHESIVES

A. *Flour pastes*

In some cases, flour pastes are preferred to those of starch because of their greater adhesiveness probably due to their protein or gluten content. Rye and wheat flours are most frequently used. We have already noted that certain wheat flours have a high gluten content. In the case of rye, a typical analysis is reported as follows: ¹

Water	10.62%
Protein	12.40%
Fat	1.65%
Carbohydrates	71.40%

Although the protein content is high, rye flour is frequently employed for poorer pastes, indicating that not only the amount but also the kind of protein present is important.

Corn and rice flours find little application as flour pastes although they contain appreciable amounts of protein.² Although cassava flour contains very little protein (2.08 per cent) ³ and is cheaper than the starch derived from it, it is not frequently used. Pastes prepared from cassava flour are less adhesive and less concentrated than those

¹ Thorpe's Dictionary of Applied Chemistry, Revised and Enlarged Edition (1929), Longmans, Green & Co., Vol. 2, p. 139.

² Thorpe's Dictionary of Applied Chemistry, 4th Edition (1939), Vol. 2, p. 481.

³ Same as 2, p. 14.

made from the starch because of the starch cellulose and other difficult soluble substances present in the flour. In addition, like all flour products, it has a greater tendency to putrefy than the starch paste.

Sago flour⁴ contains only 0.25 per cent protein. From that fact alone we may conclude that it would find little use in flour pastes.

Flour pastes find many applications among which the following may be mentioned:

1. Glueing paper and cardboard.
2. Posting bills.
3. Labelling.
4. Bookbinding.
5. Hanging wall paper.

The chief defect of flour pastes is their high water content which, at times, makes the paper pucker and increases its inclination to bacterial decomposition. Under proper conditions, paper can be stretched when moistened, and on drying gives the tautness so desirable in wall paper. For these considerations, flour pastes should be creamy, not thin and watery.

Before discussing specific formulae, the following general directions for the preparation of flour pastes would be considered.

In general, the flour is made into a smooth paste free of lumps, with twice its weight of water. Boiling water six to eight times the weight of the flour is then added while stirring. Flour pastes may be preserved with formaldehyde or zinc chloride.

Radley⁵ states that the stability of a flour paste may be improved by the addition of acetic acid. The stability of a paste appears to be directly proportional to its water hold-

⁴ Same as 1, Vol. 5, p. 14.

⁵ J. A. Radley, *Starch and its Derivatives*, Chapman and Hall, Ltd., London (1940), p. 171.

ing power which can be conveniently determined in the following way.⁶

The samples to be compared are made into mucilages of the same concentration and under identical conditions. The mucilages are allowed to cool to room temperature and when jelled, a cylinder of the same size is cut from each and stood on end on a piece of filter paper lying on a sheet of glass. The whole is covered with a bell-jar and left for several hours. At the end of this time, the diameters of the rings of moisture on the paper are compared. The one with the largest ring has the lowest water holding power and therefore would give the least stable paste. This author recommends, in principle, adding of glycerin and aluminum sulfate to these pastes.

Micksch ⁷ found that rye flour pastes prepared with hot water are 60 per cent stronger than cold mixed products. Cold mixed flour pastes should be used only when it is impossible to obtain hot water.

Flours derived from tubers such as the potato, or sweet potato are used only for low grade adhesives. These pastes tend to break down in a few hours. Syneresis, which is the scientific term for the squeezing out of water from a paste, occurs frequently.

The simplest type of flour paste is one which contains flour, water, preservative and nothing else. Standage ⁸ gives the following simple directions for the preparation of a paperhanger's paste. Beat into perfect smoothness, wheat or rye flour in a minimum of water, to produce a creamy paste. Heat just to a boil while stirring continuously. Add a little phenol as a preservative.

⁶ Same as 5, p. 185.

⁷ K. Micksch, *Taschenbuch der Kitte und Klebstoffe*, Wissenschaftliche Verlagsgesellschaft, Stuttgart (1939), p. 25.

⁸ H. C. Standage, *Cements, Pastes, Glues, Gums*, Eighth Impression, C. Lockwood and Son, Ltd., London (1931), p. 117.

We have seen, in our discussion of starches, that the addition of caustic soda or other chemicals is frequently very beneficial. The same is true of flours. Standage presents a number of formulae of this type.⁹

Billposter's Paste

Alum	1 oz.
Flour	666 oz.

The alum is dissolved in cold water and the flour is gradually added, the mixture is stirred until the paste is creamy and free of lumps. Use enough water to get a thick paste that will brush properly. This paste will not hold in damp or wet weather. After sticking the poster, to improve its moisture resistance, it is washed with soap water or a dilute lead acetate solution.

*Labelling Paste*¹⁰

Rye Flour	4 oz.
Alum	1/2 oz.
Water	8 oz.
Glycerin	1 oz.
Oil of Cloves	2 drops

Dissolve the alum in the water and rub in the rye flour until a smooth paste is obtained. Pour paste into one pint boiling water and heat until thick. Add 1 oz. of glycerin and 2 drops of oil of cloves and stir until homogeneous.

Rice flour made into a paste with hot water is said to make an excellent glue for fine paper work.¹¹

⁹ Same as 8, p. 107.

¹⁰ Same as 8, p. 111.

¹¹ Same as 8, p. 109.

Another formula involves the use of alum for a paper-hanger's paste.¹²

Paperhanger's Paste

Wheat flour	2 lb.
Water	4 qt.
Alum	1 oz.

Work the wheat flour into a batter, free of lumps, with one quart of cold water. Add 3 quarts of boiling water with active stirring and continue heating, if necessary, until the paste thickens to a semi-transparent mucilage. Finally stir in a solution of the alum in 4 fluid ounces of hot water.

*Envelope Adhesive*¹³

Potato Flour	13 kg.
Water	80 kg.
Caustic Soda (37° Bé)	3 kg.
Nitric Acid (24° Bé)	3 kg.
Formaldehyde or Phenol	1 kg.

Make a uniform paste of the starch and water. With active stirring, add the caustic soda and heat until a clear, homogeneous paste is obtained. Add the nitric acid but the paste should be left faintly alkaline to phenolphthalein (see Chapter III). Finally stir in the formaldehyde or phenol.

At times, flours as well as starches are chemically treated and dried. Such adhesives are sold as ready to use by simply mixing with cold water.

¹² H. Bennett, Chemical Formulary, D. Van Nostrand Co. (1936), Vol. 3, p. 1.

¹³ H. Bennett, Chemical Formulary, Chemical Publishing Co., Inc. (1939), Vol. 4, p. 18.

*Cold Water Paste*¹⁴

Wheat flour	8 oz.
Alum	1 oz.
Water	8 oz.

Mix until smooth, evaporate to dryness and grind.

B. Starch adhesives:

Starch pastes are among the most important of the water soluble adhesives. By a proper choice of raw materials and conditions of manufacture, a wide variety of adhesives may be obtained. The final products can be surprisingly different and may be applied in widely diverse fields. The raw materials that are most frequently used for this type are potato and cassava (tapioca) starch but the latter is generally preferred because it gelatinizes more readily, has a better odor, and produces an adhesive of greater viscosity and strength.

Radley¹⁵ gives an example of the simplest type of starch adhesive.

Cheap Starch Adhesive

Water	150 lb.
Starch	100 lb.
Caustic Soda (36° Bé)	25 lb.
Water	25 lb.
Water	550 lb.
Borax	0.14 lb.
Hydrochloric Acid (22° Bé)	5.0 lb.
Water	50.0 lb.

¹⁴ Australian Patent No. 8259.

¹⁵ Same as 5, p. 76.

The starch is stirred in cold water, and when thoroughly wet out, the diluted caustic soda solution is run in slowly. In a short time, the mass becomes an opaque, very thick paste which, on continued stirring, becomes perfectly homogeneous, transparent, very viscous, and tenacious. The temperature must be carefully maintained at 15–20°C. If the temperature is lower, the reaction is too slow; if higher, the starch tends to break down to dextrin. The reaction takes about 90 minutes but depends upon the efficiency of the stirring and the temperature. When the first step is completed, 550 lb. water, containing the borax, is run in. This is followed by the acid diluted with water. The paste should be left slightly alkaline.

There are innumerable starch adhesives. Besides differing according to their varied sources, the character of all these compounds is changed in many respects by addition of various chemicals which accommodate the adhesive to its special purpose. To have at least a superficial view of all these more or less complicated mixtures, varieties and derivatives we shall divide the additions in 5 classes:

1. *Treatment with caustic alkalis* may take place in a hot or cold state. The adhesives obtained by this treatment give strong joints and resist moisture well.

140 lb.	starch are suspended in
210 “	water and
35 “	sodium caustic (36° Bé), diluted with
35 “	water are added with constant stirring when
	the mass is thoroughly converted. Add
	slowly
550 “	water, in which is dissolved
0.14 “	borax, followed by addition of
50 “	water.

2. *Treatment with other alkaline substances:*

Painter's Glue:

100 lb. starch are treated with

14 " sodium silicate (36° Bé) and

4 " slaked lime; then a small amount of rosin soap is added.

3. *Treatment with acids:*

Transparent Adhesive for Poster Work:

Starch is suspended by stirring 1-4 and $\frac{1}{2}$ hours at 45°C. in a 1-2 per cent sulfuric acid solution. Formaldehyde is added and the suspension is heated up to 72°C. It is then filtered and dried.

4. *Treatment with salts, oxidizing or swelling agents:*

Syrupy Paste for Wallpapers:

100 lb. starch is suspended in

180 " water at room temperature and

115 " calcium chloride is added with constant stirring for 2 hours,

1 " borax is added at the end.

5. *Addition of various compounds:*

Soap, gives an unctuous consistency.

Albumin derivatives increase spreading power and elasticity, etc., etc.

More details and special formulas will follow.

Certain starches, especially cassava, absorb so much water that the paste is too viscous and tough for many applications except when diluted to an objectionable degree. For a strong, dense bond, the adhesive should be highly concentrated. The viscosity of the starch solution may be reduced by breaking the starch down to dextrin, but this reduces the bonding strength.

Perkins and Grosvenor discovered processes which reduce

the amount of water absorbed but appear to leave the starch molecule intact. We shall consider their patents in detail shortly.

Homogeneous starch pastes deposit, on standing, some white solid material which is insoluble in water and does not give a blue color with iodine showing that the substance is not starch. The phenomenon is called retrogradation of starch and is believed to be due to a reaction of some impurities found in starches. This tendency is reduced by the action of heat and oxidizing agents. Many starches, including potato, rye, wheat, barley and corn-starch, give this deposit.

*Vegetable Glue*¹⁶

Water	200 l.
Potato Starch	100 kg.
Sodium Hydroxide (35° Bé)	28 kg.

The temperature of the water should be above 16°C. Mix the starch and water and stir until a homogeneous suspension is obtained. Run in the sodium hydroxide. Continue stirring until a glassy mass is obtained. Keep the temperature low if a thick mucilage is required. Higher temperatures give more liquid glues.

*Bookbinder's Paste*¹⁷

Water	100 l.
Trisodium Phosphate	15 kg.
Borax	10 kg.
Alum	10 kg.
Starch	50 kg.

¹⁶ Same as 12, p. 5.

¹⁷ Same as 12, p. 11.

Heat the water to a boil. Dissolve the borax and trisodium phosphate in it. Add the starch, a little at a time, with continuous, efficient stirring. Maintain heat until the paste is fluid.

*Paperhanger's Glue*¹⁸

Calcium Chloride	34 lb.
Potato Starch	40 lb.
Water	2 gal.

Dissolve the calcium chloride in the water and then mix in the starch slowly until a uniform paste is formed. The paste is then dried and ground.

In some cases, a mild alkali, like sodium bicarbonate, appears to be useful in starch adhesives. Radley¹⁹ describes an adhesive of this type.

Starch Adhesives

Tapioca Starch	320 lb.
Water	500 lb.
Sodium Bicarbonate	0.65 lb.
Sodium Hydroxide (36° Bé)	80.0 lb.
Formaldehyde (30%)	6.0 lb.
Turkey Red Oil (Ammonium Salt)	0.65 lb.

The sodium bicarbonate is dissolved in the water and the tapioca is added slowly with constant stirring. The sodium hydroxide is diluted with an equal weight of water and run in slowly. The temperature is maintained at 15–20°C. throughout the reaction. The stirring is continued for 12 hours. At the end of that time, the formaldehyde and

¹⁸ Same as 13, p. 17.

¹⁹ Same as 5, p. 177.

Turkey red oil are added. The stirring is continued for another twenty minutes after which the batch is run off.

Excellent results may also be obtained with potato starch but the starch jelly is less stable and more difficult to handle. Formaldehyde is an excellent preservative, but in some cases its volatility and odor may be objectionable. In such cases it is advisable to substitute one pound of Moldex * or Dowicide A * for the formaldehyde in the formula.

In addition to the chemicals already mentioned, oxidizing agents may be used to modify starches, and to a limited degree may be added in the dry form. Dulac²⁰ gives the following formula of this type.

Starch	96 lb.
Ammonium Persulfate	4 lb.

Mix and heat 2-3 hours at 45-50°C. Starches prepared in this way are soluble in water, but as a rule are weak adhesives.

Better results are obtained by working in solution. Radley²¹ gives the following example of this kind of product.

Veneer Adhesive

Tapioca Starch	84.4 lb.
Barium Peroxide	0.5 lb.
Soda Ash	0.1 lb.
Whiting	5.0 lb.
Urea	10.0 lb.
Water	120.0 lb.
Sodium Hydroxide	2.5 lb.

* See index of trade marked products.

²⁰ R. Dulac and J. L. Rosenbaum, Industrial Cold Adhesives, Charles Griffin and Co., Ltd., London (1937), p. 113.

²¹ Same as 5, p. 175.

The tapioca starch, barium peroxide, soda ash, whiting and urea are mixed thoroughly in the dry form and added gradually to the water with constant stirring. The mass is then heated to 70°C. and when it is uniform, the sodium hydroxide, dissolved in 7.5 lb. water, is added carefully. The stirring and heating is continued until the adhesive has the desired viscosity. Sago, corn or potato starch may be substituted in the above formula.

Perkins developed two processes for modifying the properties of cassava starch so that highly concentrated, but fluid glues, could be obtained. The adhesive is prepared in two steps, the first of which is a chemical treatment and the second step which consists of bringing the starch into solution. His first process entails the use of sulfuric acid.²²

Cassava Starch	100 lb.
Water	100 lb.
Sulfuric Acid (66° Bé)	2-3 lb.

The acid is added to the water and the starch is stirred in gradually. The suspension is then heated to 55°C. and maintained at that temperature from four to six hours. After cooling, the starch is neutralized with caustic soda solution and dried. The starch may be sold in this form and prepared for use as an adhesive in the manner described below.

Acid Treated Cassava Starch ..	200 lb.
Water	225 lb. or less
Sodium Hydroxide	20 lb.
Water	30 lb.

Suspend the acid treated cassava starch in water and stir thoroughly. Add the sodium hydroxide dissolved in water

²² F. G. Perkins, U. S. Patent No. 1,020,655 (1912).

very slowly, with constant stirring over a period of 15–20 minutes.

An alternative Perkins process²³ consists of treating cassava starch with sodium peroxide.

Cassava Starch	100 lb.
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Water	100 lb.
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Sodium Peroxide	0.25–1.0 lb.
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Water	5.0 –20. lb.
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Sodium Hydroxide	0.25–1.0 lb.
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Water	5.0 –20. lb.
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Suspend the starch in water and stir thoroughly.

Add the sodium peroxide very cautiously, while stirring, to the water in a stainless steel pail. Sodium peroxide is very corrosive and also tends to spatter. Add the solution of sodium peroxide immediately to the starch suspension. The sodium hydroxide dissolved in water may be added immediately before or after the sodium peroxide.

Do not heat the mass but stir for twelve hours. Filter the starch and dry it at a low temperature.

The adhesive paste is prepared in the same way as described for the acid treated starch.

Grosvenor²⁴ obtained a similar product by a simplified, one step process.

Raw Cassava Starch (Medium Quality) .	250 lb.
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Water	800 lb.
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Sodium Hydroxide	25 lb.
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Water	75 lb.
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²³ F. G. Perkins, U. S. Patent No. 1,020,656 (1912).

²⁴ W. M. Grosvenor, U. S. Patent No. 1,200,488 (1912).

Suspend the starch in water using a strong, efficient agitator. Stir $\frac{1}{2}$ hour. Add the sodium hydroxide dissolved in water gradually over a period of about $\frac{1}{2}$ hour.

This gives a colloidal solution of starch in caustic soda, but it is too viscous. By stirring for several hours, the viscosity of the solution is gradually reduced. After five or six hours, the paste has the desired fluidity.

Many adaptations of the Grosvenor process have appeared, some of which we have already considered.

The Roger Dulac process, like the Perkins process, uses an oxidizing agent, hydrogen peroxide, but at a higher temperature. Perkins gives the following formula for the most concentrated paste of this type.²⁵

Water	600 lb.
Calcium Hydroxide	6 lb.
	8 lb.
Hydrogen Peroxide	(12 Vol.)
Cassava Starch	300 lb.
Sodium Fluoride	0.5 lb.
Formaldehyde (30%)	5.0 lb.
Sodium Fluoride	2.0 lb.
Formaldehyde (30%)	5.0 lb.
Water	1.0 lb.

The starch is suspended in cold water with an efficient agitator. The calcium hydroxide and formaldehyde are then added. The mass is heated to 85°C. for a length of time that depends upon the size of the batch and efficiency of stirring. When the glue has the desired consistency, add the sodium fluoride and formaldehyde. The formaldehyde

²⁵ Same as 20, p. 81.

reacts vigorously with the hydrogen peroxide that is in excess. The heating and stirring is continued for fifteen minutes and when the reaction has subsided, the second lot of sodium fluoride and formaldehyde is added. Finally add the water.

Sodium fluoride is a valuable preservative for vegetable adhesives. It is effective, stable, non-volatile, odorless and inexpensive. At times, soap is used to improve the dispersion, stability and adhesion of a starch paste. The following is an additional example of the Dulac process.²⁶

Water	850 lb.
Sodium Hydroxide (36° Bé)	0.45 lb.
Hydrogen Peroxide (12 Vol.)	0.35 lb.
White Soap	0.50 lb.
Cassava Starch	140.0 lb.
Sodium Fluoride	2.0 lb.
Formaldehyde (30%)	5.0 lb.
Water	3.0 lb.

The cassava starch is suspended in the water with an efficient agitator. The white soap, sodium hydroxide, and hydrogen peroxide are then added. As in the preceding example, the temperature is raised to 85°C. and maintained until the product has the desired viscosity. Finally, the solution of sodium fluoride and formaldehyde is added and the mass is mixed fifteen minutes longer. Additional soap to that given in the last formula may be used. In some cases this is as much as 14 lb.

Adhesives for use in cigarette machines must be highly concentrated and quick setting. As a final example of this class of adhesives, we have the following product.²⁷

²⁶ Same as 20, p. 80.

²⁷ Same as 20, p. 84.

Water	700 lb.
Sodium Hydroxide (36° Bé)	0.45 lb.
Hydrogen Peroxide (12 Vol.)	3.0 lb.
Cassava Starch	280.0 lb.
Hydrogen Peroxide (12 Vol.)	1.0 lb.
Water	3.0 lb.
Sodium Fluoride	2.0 lb.
Formaldehyde (30%)	5.0 lb.
Water	3.0 lb.

The cassava starch is suspended in water with an efficient agitator. After adding the hydrogen peroxide and sodium hydroxide, the mass is heated to 85°C. When the reaction has subsided, the second addition of hydrogen peroxide is made and the heating continued until the glue has the desired viscosity. Thereupon the sodium fluoride and formaldehyde solution is added and the mass is stirred fifteen minutes longer.

Sodium silicate alone is a good adhesive but combined with a tapioca starch glue it gives a more efficient compound which is inexpensive, dense and more stable on dilution than sodium silicate alone.

Tapioca Starch	130 lb.
Water	20 gal.
Sodium Hydroxide (36° Bé)	33 lb.
Water	3.3 gal.
Sodium Silicate (35° Bé)	43.0 lb.
Borax	0.1 lb.
Water	15.0 gal.
Hydrochloric Acid (22° Bé)	35.0 lb.
Water	20.0 gal.

Suspend the tapioca starch in water and run in the sodium hydroxide solution, at room temperature. When the mass is clear, add the sodium silicate and follow it with the borax dissolved in water. Add the dilute acid, when the mass is homogeneous. Test the alkalinity of the paste with phenolphthalein solution during the addition of the acid and leave the paste faintly alkaline.

There are times when a viscous, inexpensive, neutral, ropy, starch adhesive is desired. A product of this kind is prepared by treatment of starch with alkali at room temperature followed by neutralizing the alkali.²⁸

Neutral Starch Adhesive

Water	240 lb.
Starch	160 lb.
Sodium Hydroxide (30° Bé)	40 lb.
Water	320 lb.
Hydrochloric Acid (22° Bé)	31 lb.
Water	200 lb.
Formaldehyde (30%)	5 lb.
Water	5 lb.

The temperature is maintained at 15–20°C. and the stirring with the alkali is continued for about 90 minutes, until the mass is homogeneous. After diluting the paste with water, the acid is run in very carefully.

Salts are of value in starch adhesives because they increase the density, stabilize the starch paste, and reduce the tendency to gelatinize, when neutralized. Common salt may be added to a starch paste to advantage without mak-

²⁸ Same as 20, p. 64.

ing the paste hygroscopic. 24 lb. common salt may be added to the last formula. The addition is made, immediately after running in the acid, and the mass is mixed for an additional ten minutes. It should be noted that common salt is also formed whenever sodium hydroxide is neutralized with hydrochloric acid.

For a very strong glue, Dulac recommends that the hydrogen peroxide treatment be carried out at room temperature, which is strongly reminiscent of the Perkins sodium peroxide process.²⁹

Wood Glue Adhesive

Water	500.00 lb.
Sodium Bicarbonate	0.65 lb.
Cassava Starch	320.00 lb.
Hydrogen Peroxide (12 Vol.)	10.00 lb.
Sodium Hydroxide (36° Bé)	80.00 lb.
Water	80.00 lb.
Turkey Red Oil	
(Ammonium Salt, 90%)	0.65 lb.

The cassava starch, water, hydrogen peroxide and sodium bicarbonate are mixed at room temperature. The diluted sodium hydroxide is then added and the mass is stirred for twelve hours. The paste is stirred twenty minutes longer after adding the Turkey red oil.

Numerous chemicals, far too many to mention, have been used to modify starches so as to cause their swelling in cold water. We can review only a few of the more practical formulae.

Neustadt³⁰ patented the following formula:

²⁹ Same as 20, p. 111.

³⁰ G. P. Neustadt, German Patent No. 392,660 (1921).

Potato Starch	100 kg.
Calcium Nitrate	3 kg.
Sodium Chloride	1.5 kg.
Magnesium Sulfate	1.5 kg.

Dissolve the above chemicals in a minimum of water, dry, and grind the dried powder.

Urea is used in the manufacture of starch adhesives as well as in casein and gelatin glues. It reduces the viscosity of the paste so that glues of higher concentration can be made without change in working properties. It increases setting time a little which is an advantage in some cases, but it does not increase the drying time.

Furthermore, it is claimed that urea strengthens the glue and is particularly useful for non-rigid joints. Finally, urea solubilizes the compound formed by the reaction between formaldehyde and starch.

A defect of some modified starches that swell in cold water is that, when finely ground, they tend to form lumps on dissolving in water and, when coarsely ground, they take many hours to swell.

Kantorowicz ³¹ patented the use of sodium phosphate, as given below, to produce a non-lumping starch:

Potato Flour	100 kg.
Water	100 l.
Sodium Phosphate	3 kg.

Mix into a uniform paste. Dry on a hot surface and grind. Soluble albumins, gums, dextrans and pectins have also been used to improve the wetting of modified starches.³²

During the past ten years the U. S. Department of Agri-

³¹ J. Kantorowicz, U. S. Patent No. 1,677,348.

³² German Patent No. 389,023.

CHAPTER V

DEXTRIN ADHESIVES

AGRICULTURAL products are rarely, if ever, as uniform as those produced synthetically. Soil, climate, weather, insects, etc., contribute in making one corn crop a little different from another. These variations are passed on to the starch and then to the dextrin produced from it. Important differences in dextrans result from the kind of starch used (i.e. corn, wheat, potato starch, etc.) and from the details of the manufacturing process.

Starch is converted into dextrans in 3 ways:

- a. Dry roasting at about 200°C. gives dark, soluble "British Gums."
- b. Roasting after mixing in an acid which works as catalyst (promotor of the process); e.g., for 100 lb. starch 6 ounces hydrochloric acid in 2 gallons of water are spread on. Roasting temperature varies according to the kind of starch;

Tapioca	140-175°C.
Maize	125-140°C.
Potato	105-135°C.

Various chemicals are added to dextrans to improve their properties. Because of their greater solubility, dextrans replace starch adhesives where very rapid setting is required. We do not except high resistance to water.

As a rule, dextrans are slightly acid from the roasting process. In acid solution dextrans may be a trifle clearer but their adhesive strength is reduced. On addition of

alkali, dextrin solutions are darkened but become more viscous and sticky. Borax and caustic soda are most frequently used. The former discolors the dextrin solution less whereas the latter gives the adhesive a vitreous and ropy character. Much larger amounts of borax are required with dextrin than with starch and the effect on yellow dextrans is less than on the white. The addition of borax increases the density of the adhesive and therefore reduces the drying time. It also improves the stability of the paste and reduces the cost.

In many cases, both caustic soda and borax are used since the strongest adhesive is obtained in this way. The brown color caused by caustic soda is least pronounced in the presence of borax *which must always be added first and completely dissolved* before the caustic is added. Generally, twice as much borax as caustic soda is used and the total weight of these chemicals often amounts to 15% of the weight of the dry material present.

Dextrin breaks down on heating in the same way as starch and therefore as little heat as possible, for as short a time as possible should be used in preparing dextrin adhesives.

It is common practice to add sodium bisulfite to mask the odor and to act as preservative and bleach.

Simple dextrin solutions are infrequently used as adhesives but we may record a few formulae of this type.¹

Photo Paste

Dextrin, White	24 kg.
Water	24 l.
Ginger Grass Oil	10 gm.

¹ Bennett, H., Chemical Formulary, Vol. 5, p. 17, Chemical Publishing Company, Inc. (1940).

The dextrin is dissolved in the water with a gentle heat. The oil is then stirred in.

The following formula ² is an example of an ordinary alkaline dextrin paste:

Water	500 gm.
Ordinary Soluble Dextrin	390 gm.
Borax	46 gm.
Sodium Hydroxide (30° Bé)	6 gm.
Sodium Bisulfite	4 gm.

Make a thick paste of the dextrin and half the water and rub until all the lumps are gone. Mix in the rest of the water and heat to 85°C. Add the borax and stir until dissolved. Then add the sodium hydroxide and finally, with the temperature still at 85°C., add the sodium bisulfite.

The following formula ³ produces a quick setting, machine adhesive for sealing wrappers:

Water	50.0 lb.
Yellow Dextrin (Very Soluble)	40.0 lb.
Borax	40.0 lb.
Sodium Hydroxide	2.0 lb.
Phenol	0.1 lb.
Turkey Red Oil	0.5 lb.

Dissolve the dextrin in 45 lb. water, using heat, if necessary. Add the borax and stir until dissolved. Dissolve the sodium hydroxide in 5 lb. water and add it to the dextrin with rapid stirring. Then mix in the phenol and the Turkey red oil.

² Dulac, R. and Rosenbaum, J. L., *Industrial Cold Adhesives*, p. 93, Charles Griffin & Co., Ltd., London (1937).

³ J. A. Radley, *Starch and Its Derivatives*, p. 192, Chapman & Hall, Ltd., London (1940), p. 192.

Wrapping paper is relatively impervious to the adhesive but in spiral tubes the paper is more absorbent and therefore the adhesive must be a little denser. The same formula as the previous one is used except that three pounds less of water are required.

In the last formula, Turkey red oil is used to plasticize the film and is satisfactory in many cases because it is not particularly hygroscopic. Glycerin and diethylene glycol should not be used in machine adhesives because they cause difficulties in humid weather. Sorbitol (syrup) or Yumidol are very much better in this respect.

Some consumers prefer the body and working properties of an adhesive prepared from a mixture of starch and dextrins. The following formula is given by Dulac.⁴

Water	600 lb.
Turkey Red Oil (Ammonium Salt) .	2 lb.
White Dextrin (Slightly Soluble) ..	180 lb.
Light Yellow Dextrin (Soluble) ...	150 lb.
Cassava Starch	60 lb.
Borax	46 lb.
Sodium Hydroxide	6 lb.
Sodium Bisulfite	4 lb.

Make a thick paste of the dextrins and the starch with 300 lb. water. Mix in the Turkey red oil and then 280 lb. water. Heat to 85°C. with stirring. When the mass is gelatinized, add the borax. When the latter is completely dissolved, add the sodium hydroxide dissolved in 20 lb. water. The temperature is maintained at 85°C., the sodium bisulfite is added last and the mass is stirred until it is completely dissolved.

⁴ Same as 2, p. 94.

We have seen that sodium bisulfite is used for bleaching sodium persulfate and hydrogen peroxide are much more effective bleaching agents. Sodium perborate should be added at below 35°C. after all the other ingredients are in. The amount of perborate used should be deducted from the borax. Sodium perborate does not affect the viscosity of the solution whereas hydrogen peroxide and sodium persulfate reduce it. The viscosity of a dextrin solution may also be reduced by heating it with formaldehyde.

When the surfaces to be glued are very sensitive to alkali, such as certain colored papers, an absolutely neutral adhesive is required, but for satisfactory results, such an adhesive must be highly concentrated. Under these conditions, formaldehyde is used to reduce the viscosity of the paste to a workable condition. The following formula is given by Dulac: ⁵

Water	370.0 lb.
Turkey Red Oil (90%) (Ammonium Salt)	1.3 lb.
Light Dextrin (Water Soluble)	630.0 lb.
Sodium Hydroxide (36° Bé)	3.0 lb.
Formaldehyde (30%)	6.3 lb.

The mixture of water, dextrin and Turkey red oil is heated to 80°C. Add just enough sodium hydroxide (36° Bé) to neutralize the acid in the dextrin. This is determined by testing with litmus paper. About 3 lb. are required. The formaldehyde is added last.

The formaldehyde does not darken the solution nor does it destroy any of its desirable characteristics.

The following formula ¹ is for a somewhat similar library paste:

⁵ Same as 2, p. 102.

White Dextrin	10 oz.
Potato Starch	10 oz.
Water	7 oz.
Glycerin	3 oz.
Phenol	2 g.
Formaldehyde (30%)	1/8 oz.
Sassafras Oil	1 g.

Form a smooth paste with the dextrin, starch, and half of the water required. Add the rest of the water and heat on a steam bath until smooth. Stir in the glycerin, phenol, formaldehyde, and the sassafras oil.

The addition of soluble calcium salts produces a fatty paste. Both glycerin and calcium chloride make the adhesive slow drying, which is desirable for highly calendered papers that are slow to wet out. The following white paste is an example of this type: ⁶

Potato Dextrin	100 gm.
Water	150 cc.
Calcium Nitrate	10 gm.
Phenol	2 gm.

Dissolve the calcium nitrate in the water heated to 75°C. Add the dextrin a little at a time while stirring. When everything is in solution, add the phenol.

For gummed paper, the adhesive should be flexible and readily soluble on wetting. The following formula is described as giving a suitable adhesive: ⁷

Water	600.0 lb.
Dextrin (Extra Soluble)	400.0 lb.
Turkey Red Oil (90%) (Ammonium Salt)	0.4 lb.

⁶ Mieksch, K., *Taschenbuch der Kitte und Klebstoffe*, p. 21, Wissenschaftliche Verlagsgesellschaft, Stuttgart (1939).

⁷ Same as 2, p. 104.

Formaldehyde (30%)	120.0 lb.
Gelatin	20.0 lb.
Glycerin	40.0 lb.

Soak the gelatin in 100 lb. water over night. Next day heat it to 80°C. with stirring. Add the glycerin and stir until uniform.

Add the dextrin and Turkey red oil to 500 lb. water and heat to 80°C. with stirring. Add the gelatin, glycerin solution which has been previously prepared and stir 15 minutes longer.

Other salts besides those of calcium are used sometimes. The use of aluminum sulphate is recommended in the following paste for paper to metal foils.⁸

(a) Dextrin	40 gm.
Glucose	1 gm.
Water	40 gm.
(b) Aluminum Sulfate	1 gm.
Water	30 gm.
(c) Glycerin	3 gm.

Dissolve (a) and (b), and mix them. Heat until clear. Add (c) and mix.

Some dextrin adhesives are put on the market in powder form. The following formula is a typical example:⁹

Dextrin	100.0 lb.
Borax	120.0 lb.
Sodium Carbonate	1.2 lb.

The powders are mixed thoroughly. The resulting powder is mixed with one and a half times its weight of water on the evening before the day it is to be used.

⁸ Same as 1, p. 18.

⁹ Same as 2, p. 99.

Another example, suitable for dentures is described by Radley:¹⁰

Tapioca Dextrin (Soluble, Pure) ..	20.0 lb.
Casein (Finely Powdered)	10.0 lb.
Borax	0.1 lb.

Mix thoroughly.

Dextrins are sometimes mixed with sodium silicate to produce an adhesive that has some of the strength of a silicate bond. The following is a typical formula:¹¹

Water	90.00 l.
Dextrin (White)	30.00 kg.
Dextrin (Yellow)	100.00 kg.
Glucose (Syrup)	20.00 kg.
Sodium Silicate (38–40° Bé) ...	0.25 kg.
Sodium Bisulfite (36–40° Bé) ..	0.50 kg.

Mix the dextrins with cold water and stir until free of lumps. When homogeneous heat gently, with stirring, but do not boil. Stir until a clear solution is obtained. Cool to 70–75°C. and add the glucose, sodium silicate and sodium bisulfite.

It is reported that the adhesive properties of dextrins are improved by the addition of urea.¹²

Other references:

National Adhesives Company, E.P. 383,778.

Radley, J. A., *Starch and its Derivatives*, p. 148, Chapman & Hall, Ltd., London (1940).

¹⁰ Same as 3, p. 196.

¹¹ Same as 1, p. 36.

¹² German Patent 605,016.

CHAPTER VI

CASEIN ADHESIVES

IN CHAPTERS IV and V, we have considered flour, starch and dextrin adhesives and have seen that their chief defect is their more or less permanent solubility in water. Casein adhesives are used whenever a strong, waterproof glue is required but have one important disadvantage. Casein glues are not stable in solution for any length of time if they are really water resistant. Generally glues of this type are prepared from the powder a short time before they are to be used.

Water resistance is less a question of the amount of water absorbed by the adhesive as it is of the decrease in strength caused by the water. Water resistance does not depend on the chemical structure but on the physical state. Various factors cause the irreversibility of the gelatin.

Casein glues, like other alkaline glues and animal glues are hygroscopic but do not lose their strength in high humidities as quickly as do animal glues. Some consumers prefer to buy their casein glues prepared for mixing with water. These glues contain all of the required ingredients and must merely be mixed with water at room temperature, generally in the ratio of two parts of water to one of glue. The glue can be prepared in less than thirty minutes but must be used in a day or less. There are a number of advantages in buying glues in this form. In the first place, only one product has to be bought and tested. Secondly, only one weighing need be made which saves time and reduces the number of possible errors.

For the big consumer, the preparation of glues, direct

from their ingredients, offers possible economies and the advantage of flexible formulation of glues to meet changing requirements.

Casein glues may be classified in two groups: a. glues giving reversible jellies; b. glues giving irreversible jellies. The first group, the less important one, is not waterproof, but is more stable than the second, which is waterproof to some extent. Products may be prepared which lie between these extremes and possess some of the properties of each.

Casein is insoluble in water and is brought into solution with the aid of alkalis. As we know, the viscosity of an adhesive must vary with its application. In casein glues, viscosity can be varied by changing the concentration and by varying the kind and amount of alkali used. By proper formulation, the consistency of casein glues can be varied from a thin watery type to a molasses-like thickness. When alkalis such as sodium hydroxide or ammonium hydroxide are used alone, the casein glue is as strong as animal glue but, in this case, it is not water resistant.

The viscosity of a casein glue is reduced by increasing the amount of alkali. A strong alkali gives a more fluid glue than a weak one. Thus, a glue made with sodium hydroxide is thinner than one prepared with a chemically equivalent amount of ammonium hydroxide.

Sutermeister¹ gives the following examples of this type of glue:

1. Casein	100 gm.
Water	280 cc.
Sodium Hydroxide	8 gm.
Water	20 gm.

¹ Sutermeister, E. and Brown, F. L., p. 242, *Casein and its Industrial Applications*, 2nd Ed. (1939), Reinhold Publishing Corp.

Stir the casein in the first quantity of water for five to ten minutes. Add the sodium hydroxide, dissolved in the second quantity of water, and stir from thirty minutes to an hour:

2. Casein	100 gm.
Water	580 cc.
Ammonium Hydroxide (28-29% Ammonia)	13 cc.
Water	20 cc.

As in the first example, the casein is stirred in the first quantity of water and then the diluted ammonium hydroxide is added. Stirring is continued until a clear solution is obtained.

These two glues have the same viscosity although the second contains twice as much water as the first. This illustrates the importance of the kind of alkali used. 2. is used when less glue per given area of joint is desirable or longer storage needed; to avoid the deteriorating influence of sodium hydroxide, glues of this formula are prepared:

Casein	100 parts
Calcium Hydroxide	7 parts
Sodium Carbonate in proportion	

Irreversible jellies can be obtained by using formaldehyde to harden the casein (this has not proven practical as far as adhesives are concerned, or by introducing into the compound water resistant calcium caseinate (adding calcium hydroxide). There are many varieties of this basic compound.

In the following example both sodium hydroxide and calcium hydroxide are used: ²

² Thorpe's Dictionary of Applied Chemistry, p. 411, Vol. 2, 4th Ed. (1939), Longmans, Green & Company.

Casein	7.5 gm.
Sodium Hydroxide	1.0 gm.
Water	30.0 cc.
Calcium Hydroxide	1.5 gm.

The casein is thoroughly wet out with 25 cc. water. After ten minutes, the sodium hydroxide dissolved in 5 cc. water is added and the solution is stirred until clear. Finally, the calcium hydroxide is mixed in. The chief defect of an adhesive of this type is its strong alkaline reaction resulting from the sodium hydroxide. A very strong glue can be prepared without caustic soda but in this case, the glue is usable for only a half hour after it is mixed:

Casein	10 gm.
Calcium Hydroxide	2 gm.
Water	40 gm.

The casein and calcium hydroxide are stirred into cold water and the adhesive is ready for use. The last formula gives a glue which is very waterproof.

The length of time that a casein glue, in solution, is usable depends upon two factors. The higher the proportion of caustic soda, the longer it can be used. The higher the proportion of calcium hydroxide, the shorter the working life of the glue. However, the more calcium hydroxide there is present, the more waterproof the glue. In other words, a compromise must be made between maximum water resistance and a reasonable working life for the glue.

Prepared casein glues in powder form cannot be made with caustic soda because of its hygroscopic nature. The caustic soda can be replaced by sodium carbonate, borax or trisodium phosphate in accordance with the following formulas:

Casein	100.0 gm.
Borax	14.7 gm.

Grind and mix thoroughly.

Casein	100.0 gm.
Trisodium Phosphate	12.3 gm.

Grind and mix thoroughly.

Casein	100.0 gm.
Soda Ash	16.0 gm.

Grind and mix thoroughly.

In each of the above cases, the powder is mixed with from four to six parts of cold water for use.

We have seen above an example of a glue in which both calcium hydroxide and sodium hydroxide were used. In the following example, to reduce alkalinity, calcium chloride is used: ³

Casein	100 gm.
Water	250 gm.
Sodium Hydroxide	11 gm.
Calcium Chloride	20 gm.

The casein is soaked in 180 gm. water with stirring. The sodium hydroxide is dissolved in 50 cc. water and is added to the casein. When the casein is completely dissolved, add the calcium chloride dissolved in 20 cc. water. Stir for a few minutes. The glue is then ready for use. It remains fluid for seven hours.

Strong alkalis such as sodium hydroxide discolor wood. Therefore, their use in glues for veneer and plywood is objectionable.

A combination of calcium hydroxide and ammonium

³ Hadert, H., p. 52, Kaseinleim und Kaseinfarben-Bindemittel, 2nd Ed. (1937).

hydroxide is impractical because the working life of the glue is very short.

We shall see that many formulas require the use of sodium fluoride. There are some who say that no good casein glue can be made without it.

It dissolves casein more rapidly than trisodium phosphate and reduces the alkalinity of the glue. As a result, the casein decomposes more slowly and stains wood less. Sodium Fluoride seems to increase the stickiness of the glue. Care must be taken in using glues containing large quantities of sodium fluoride because of the danger of serious skin eruptions if handled carelessly.

Sodium fluoride is frequently used to replace the caustic soda.

Casein	100 gm.
Calcium Hydroxide	30 gm.
Sodium Fluoride	12 gm.
Water	250 cc.

The first three ingredients are stirred into the cold water and the glue is ready for use in a few minutes.

Hadert offers a number of variations of glues containing sodium fluoride which are presented below.⁴

The following glue foams very little:

Casein	70 kg.
Trisodium Phosphate	10 kg.
Calcium Hydroxide	20 kg.
Sodium Fluoride	3 kg.
Water	200 l.
Pine Oil	2 kg.

The casein is soaked in the water for ten minutes and then the other ingredients are added in order, with stirring.

⁴ Same as 3, p. 77.

The following adhesive is prepared in powder form. It is a strong furniture glue and discolors only the most sensitive woods. It can be used for 6–8 hours after mixing with about three parts of cold water.

Casein	50.0 kg.
Calcium Hydroxide	5.0 kg.
Calcium Carbonate	10.0 kg.
Disodium Acid Phosphate	5.0 kg.
Sodium Fluoride	5.0 kg.
Mineral Oil	2.5 kg.

The mineral oil is added to keep the powder from dusting.

The following is a formula for a strong veneer glue that brushes well and does not set too quickly. It is useful for work with large areas:

Casein	69 kg.
Calcium Hydroxide	20 kg.
Sodium Fluoride	5 kg.
Sodium Sulfite	3 kg.
Mineral Oil	3 kg.

Among the strongest glues obtained from casein are those that contain sodium silicate. Silicated glues, at times, become so hard that they injure steel cutting tools. In the presence of sodium silicate, casein is not affected by calcium hydroxide as rapidly and the working life of the glue is prolonged. These adhesives have excellent water resistance. A glue of this type can be made from the following formula: ⁵

⁵ Forest Products Laboratory, Casein Glues, Their Manufacture, Preparation and Application, Mimeograph R 280 (1935).

Casein	100 lb.
Water	350 lb.
Calcium Hydroxide	32 lb.
Sodium Silicate	70 lb.

The casein is soaked and stirred in 250 lb. water. The calcium hydroxide is stirred up in 100 lb. water and is added to the swollen casein. After stirring until the solution is uniform, add the sodium silicate and stir ten minutes longer. The working life of this glue is 11 hours.

The life of this glue can be prolonged, by the addition of copper chloride as given in the following formula: ⁶

Casein	100 lb.
Water	350 lb.
Calcium Hydroxide	22 lb.
Sodium Silicate	70 lb.
Copper Chloride	2-3 lb.

The procedure is the same as in the preceding example except that the copper chloride is dissolved in 30 lb. water which is deducted from the water used for soaking the casein. The specifications for the sodium silicate are the same as previously given. The sodium silicate must be added after the calcium hydroxide has reacted with the casein. The copper chloride solution is added last. The glue, at first, turns green when the copper salt is added. After a few minutes, the color turns violet and the glue is ready for use. This product is very resistant to water.

In manufacturing plywood, it is important that the glue does not set too quickly in order to give time to cover all the surfaces of the wood to be glued and transfer them to the press. The following formula produces a suitable glue for this work: ⁷

⁶ Same as 3, p. 57.

⁷ Same as 3, p. 76.

Casein	100 kg.
Water	350 kg.
Calcium Hydroxide	10 kg.
Sodium Silicate	15 kg.

The glue is prepared in the manner described above, and forty minutes to two hours may elapse between application and pressing.

The following is an example of a water resistant label glue: ⁸

Casein	20 oz.
Ammonium Hydroxide (sp.gr. 0.019)	5 oz.
Sodium Silicate (30° Bé)	6 oz.
Water	70 oz.

The casein is soaked in the water as usual. The ammonium hydroxide is then added and when the casein is in solution, the sodium silicate is stirred in.

It is claimed that the adhesive strength of a casein glue is improved by the addition of substantial amounts of clays and other inert materials. The following formula is an illustration: ⁹

Casein	100.00 kg.
Sodium Fluoride	18.75 kg.
Zinc Oxide	1.25 kg.
China Clay	30.62 kg.
Bentonite	30.62 kg.
Calcium Hydroxide	43.75 kg.
Water	450.00 kg.

⁸ Bennett, H., p. 12, *Chemical Formulary*, Vol. III, D. Van Nostrand Company (1936).

⁹ Dike, T. W. to I. F. Laucks, Inc., U. S. Patent 2,016,707.

The dry materials are thoroughly mixed and are added to the water in an efficient glue mixer.

Hadert gives another example of a glue containing an inert pigment: ⁷

Casein	50.0 kg.
Calcium Hydroxide	10.0 kg.
Trisodium Phosphate	7.0 kg.
Sodium Fluoride	3.3 kg.
Barytes	10.0 kg.
Petroleum	2.0 kg.

This glue is prepared for use by adding the mixed powder to about five parts of water in an efficient glue mixer.

In some cases, a dry method is employed in which case the surfaces are covered with the glue, allowed to dry, and then are joined by pressing in a heated press. The following formula is used for this type of work: ¹⁰

Casein	100 lb.
Calcium Hydroxide	18 lb.
Soda Ash	5 lb.
Sodium Fluoride	7 lb.
Sodium Silicate	43 lb.

The dry materials are mixed thoroughly and are stirred into the sodium silicate in an efficient mixer.

Urea is recommended as a neutral solvent for casein. A neutral solution that keeps for 2-4 days can be prepared in the following manner: ¹¹

¹⁰ Dulac, R. and Rosenbaum, J. L., p. 113, *Industrial Cold Adhesives*, Charles Griffin and Co., Ltd., London (1937).

¹¹ Shisler, G., U. S. Patent 1,886,750 (1932).

Casein	100 kg.
Urea	100 kg.
Water	75 kg.

Do not heat, as casein dissolves more slowly in a urea solution at elevated temperatures. However, it may be heated cautiously to 60–70°C. for a short time (10–15 min.) to hasten the solution of the casein.

If a water suspension of latex is added to this formula, a good adhesive for “Cellophane” is obtained.

Durham patented the use of dry milk in place of casein.¹²

Patents have been issued on the addition of inert materials such as cork and asbestos as well as the substances already mentioned.

Wetting, emulsifying and dispersing agents improve the stability of the casein glue and in the dry glueing process, they also improve the adhesion. Generally, 0.5–1.0 kg. of the wetting agent is used for 100 kg. dry glue. It is important to pick an agent that is as stable as possible in the presence of lime and alkali. Numerous products of this type are sold under trade marks among which we can mention the following: “Gardinols”, “Santomerse”, “Wetanol”, and “Sulfatate”.

A number of proprietary compounds are recommended for plasticising casein adhesives Plasticizer 11 and 22, Protoflex in addition to those already mentioned in the text. Triethanolamine is an organic amine and is used in casein glues both as solvent and plasticiser.

Miscellaneous ingredients of casein glues:

Carbon disulfide increases the water-resistance and the strength of the joint.

Mineral oils prevent dusting of the dry powder during handling and mixing.

¹² Durham, H. W., U. S. Patent 1,971,522 (1934).

Mixtures of casein have been made with:

animal glue;

blood albumin;

meals of soybean, peanut or cottonseed;

rubber latex;

synthetic resins.

Casein glues are subject to two types of decomposition. The first is chemical and depends upon the composition of the glue and the second is bacterial and can be reduced or prevented by the addition of preservatives such as phenol, thymol, "Dowicide A", or "Moldex".

CHAPTER VII

VEGETABLE GLUES

IN DISCUSSING vegetable glues, we should include flour, starch and dextrin adhesives. These products, however, are so important technically and are transformed in so many different ways, that their properties were discussed in separate chapters. The glues that we shall now consider are made from various gums found in nature.

The most important product of this group is gum arabic or gum acacia, as it is sometimes called. Chemically this gum can, in a sense, be compared with starch. Like starch, it has a large, complicated molecule which is built up from smaller units, however, these are different from the building blocks in starch. Again, like starch, the molecule tends to break down when heated in water, and if subjected to too high a temperature or for too long a time. This breakdown usually results in a drop in the viscosity of the solution and loss in its adhesive strength.

Gum arabic glues are quite easy to prepare. They are light in color, odorless, stable and are extensively used on paper but for very little else. Due to the rapid improvement in dextrans, gum arabic is now relatively unimportant. The adhesive strength of the gum can be improved by the addition of certain metal salts, such as calcium nitrate and aluminum sulfate.

By itself, gum arabic gives a very brittle film and generally 8–10% glycerin of the weight of dry gum is added to make it flexible. Instead of glycerin, diethylene glycol, ethylene glycol, sorbitol or Yumidol may be used. The gum should be dissolved in cold, soft water. If hot water

is used to hasten solution, the gum tends to break down, as we have seen above. In this decomposition an acid substance is formed which reduces the adhesive strength of the glue. In addition, the acid will discolor bronze and certain colored papers.

Depending on its quality, gum arabic is dissolved in two to three parts of water. More dilute solutions can be used if a substance that increases viscosity is added. Such products are gelatin, gum tragacanth or methyl cellulose.

Gum arabic is not inclined to ferment and even a little calcium hydroxide and glycerin is generally enough to protect it.

The following formula represents the simplest type of gum arabic glue:

Water	250.0 gm.
Calcium Hydroxide	0.2 gm.
Glycerin	8.0 gm.
Gum Arabic	100.0 gm.

The ingredients are added in the order mentioned to the cold water, with stirring. When everything is dissolved, the solution is allowed to stand in order to settle and clear. Supernatant liquid is filtered.

The following formula illustrates the addition of aluminum sulfate to increase its adhesive strength: ¹

Gum Arabic	100.0 gm.
Calcium Hydroxide	0.2 gm.
Water	300.0 cc.
Aluminum Sulfate	10.0 gm.

Dissolve the gum arabic in 200 cc. cold water. Let the solution settle and filter the clear top liquid. Add the

¹ Mietsch, K., p. 256, Taschenbuch der Kitte und Klebstoffe. Wissenschaftliche Verlagsgesellschaft, Stuttgart (1939).

aluminum sulfate dissolved in 100 cc. water. Aluminum sulfate also decreases blotting when gum arabic glue is used on paper which has not enough size.

The following two formulas have been recommended for "Cellophane" glues: ^{2, 3}

Formula I

Gum Arabic	17.50 oz.
Water	15.50 oz.
Glycerin	30.00 oz.
Formaldehyde	0.05 oz.

Formula II

Gum Arabic	16.5 oz.
Water	15.5 oz.
Glycerin	20.5 oz.
Glyceryl Bori-borate	9.0 oz.
Formaldehyde	4.5 oz.

In order to reduce the cost of a glue, a more dilute solution of gum arabic may be used and the drop in viscosity corrected by the addition of a thickening gum such as gum tragacanth.

It should be noted that the viscosity of the following glues is good although the ratio of water to gum is much higher than three to one:

Transparent Cement ⁴

Glycerin	4 oz.
Gum Arabic	4 oz.

² Bennett, H., Chemical Formulary, Vol. 5, p. 17, Chemical Publishing Co. (1940).

³ Same as 2, Vol. 3, p. 9.

⁴ Same as 2, p. 42.

Gum Tragacanth (Powdered)	1 oz.
Distilled water	32 oz.

The gum arabic is dissolved in half the water and the gum tragacanth in the other half. Gum tragacanth should not be added to hot water because it gelatinizes so readily that lumps will form, swollen on the outside but with un-wet powder in the interior. Such lumps are very difficult to eliminate.

The powdered gum tragacanth should be added to cold water with active stirring. After standing over night, the gel is stirred until it is of uniform consistency and added to the filtered gum arabic solution. Glycerin is then added and the glue is stirred until homogeneous.

A similar but more water resistant glue is prepared in the following manner: ⁵

Gum Arabic	20 gm.
Aluminum Sulfate	2 gm.
Gum Tragacanth (2% Solution) ...	15 cc.
Water	63 cc.

The gum arabic and aluminum sulfate are dissolved in water and as usual, after settling, the solution is filtered and the gum tragacanth is stirred in.

A strongly alkaline solution of gum arabic has been patented for use on greasy or waxed paper.⁶ The following formula should be used with caution because its strong alkalinity will weaken paper or cloth:

Gum Arabic	40 oz.
Potassium Hydroxide	34 oz.
Water	75 oz.

⁵ Bennett, H., Chemical Formulary, Vol. 3, p. 7, D. Van Nostrand Co. (1936).

⁶ U. S. Patent 1,983,650.

The potassium hydroxide is dissolved in the water. The solution, spontaneously, becomes very hot and should be allowed to cool to room temperature before the gum arabic is added. This glue is very caustic.

Gum arabic may be combined with flour, starch and dextrins as the following examples show:

*Postage Stamp Adhesives*⁷

Gum Arabic	100.0 kg.
Sodium Chloride	2.5 kg.
Glycerin	2.0 kg.
Starch	2.0 kg.
Water	130.0 l.

The starch is made up into a paste with 30 liters water and is heated on a steam bath until completely dissolved and a clear solution is obtained. After cooling, it is added to the filtered solution of gum arabic, sodium chloride and glycerin in water and stirred until the glue is homogeneous. Potato or tapioca starch is preferred.

*Library Paste*⁸

Flour	16.0 gm.
Gum Arabic	12.0 gm.
Gum Tragacanth	3.0 gm.
Salicylic Acid	0.5 gm.
"Clovel"	0.6 gm.
Water	160.0 cc.

⁷ Bennett, H., Chemical Formulary, Vol. 4, p. 19, Chemical Publishing Co. (1939).

⁸ Bennett, H., p. 10, Chemical Formulary, Vol. 1, Chemical Publishing Co. (1933).

The flour, preferably wheat, is made into a paste with 100 cc. water and is heated on a steam bath with good stirring until completely gelatinized. The gum tragacanth is dissolved in 30 cc. water, in the manner described above. The gum arabic is dissolved in 30 cc. water and filtered. The cold solutions of the gums and flour are combined and the salicylic acid and "Clovel" are stirred in.

Mounting Paste ⁸

White Dextrin	1 lb.
Gum Arabic	1 oz.
Water	1½ pt.
Acetic Acid	1 oz.
Oil of Wintergreen	20 drops
Oil of Cinnamon	20 drops
Salicylic Acid	20 gm.

The gum arabic is dissolved in ½ pt. water and is filtered after settling. The dextrin is stirred into 1 pt. water and heated on a steam bath until dissolved. The cold solutions of dextrin and gum arabic are combined and the acetic acid, salicylic acid and the perfume oils are then stirred in.

Paste of extraordinary adhesive power:

- 4 parts of Gum Arabic, dissolve in not too much water; heat solution and pour slowly into a mixture of:
- 3 parts of wheat starch and
- 1 part of sugar
- suspended in a little water stir and add some salicylic acid.

Lunel's paste: (for artificial flowers)

- 2 parts Gum Arabic
- 2 parts rye flower

1 part sugar

heat and stir in water until a viscous homogeneous paste results.

Gum arabic is sometimes used as a binder for fairly water resistant cements. The following examples illustrate this application:

Grey Cement ⁹ (used to fill holes in cast iron)

Gum Arabic	12 gm.
Gypsum	12 gm.
Iron Filings	12 gm.
Silica (Powder) or glass-powder ...	64 gm.

The ingredients are mixed together thoroughly. The powder is mixed into a heavy paste with cold water just before it is to be used. "Cellite", a convenient form of finely divided silica, may be used in this formula.

Iron Cement for Castings ¹⁰

Iron Filings	128 lb.
Plaster of Paris	20 lb.
Whiting	8 lb.
Gum Arabic	8 lb.
Carbon Black	1 lb.
Portland Cement	4 lb.

The ingredients are mixed thoroughly and added to cold water directly before using.

⁹ Same as 7, p. 24.

¹⁰ Same as 8, p. 7.

CHAPTER VIII

ANIMAL GLUES

GELATIN and glue do not dissolve readily in water. They swell in cold water and are finally dispersed by heat and stirring. For liquid glues, it is necessary that some decomposition takes place at this stage as, otherwise, the glue will set on cooling.

Glues are bleached, at times, with sulfur dioxide or sodium bisulfite. For more alkaline glues hydrogen peroxide is frequently used. Some manufacturers prefer to use zinc dust and sodium bisulfite or sodium hydrosulfite as a bleach.

Gelatins and glues are not water resistant. In this respect, they are a little superior to some dextrin or starch pastes but they are very much inferior to a waterproof casein glue.

Animal glues can be made more insoluble and water resistant with the aid of certain chemicals such as formaldehyde, hexamethylenetetramine, aluminum sulfate or sodium bichromate. The process is similar to the tanning of leather and any tanning agent will insolubilize a glue.

In practice, there are two ways of making a glue insoluble. The less desirable procedure is to apply the glue to the wood and before the glue is dry to apply the insolubilizing solution on it. The surfaces to be joined are then set together. In the preferred method, the insolubilizing substance is mixed with the glue under such conditions that no reaction occurs until the glue is applied. Formaldehyde is most frequently used for this purpose, about 1% on the weight of dry glue. Together with the formaldehyde, one must use some substance to slow up its reaction with

gelatin. Ammonium sulfocyanide, acetic acid and ammonium hydroxide are used for this purpose. The acetic acid and ammonium hydroxide evaporate as the glue dries which enables the formaldehyde to act. A similar situation exists when alum is used with acetic acid. One of the best ways of making waterproof glue is to use hexamethylenetetramine. This compound gives off formaldehyde when warmed gently.

If the joint is to be made by cold pressing and a combination of formaldehyde with ammonium sulfocyanide or acetic acid is used, the chemicals should be used in the following proportions:

1 part formaldehyde (30%) to 2 parts ammonium sulfocyanide or 5 parts acetic acid.

The sulfocyanide should be added to the glue first and then the formaldehyde diluted with half its volume of water.

Liquid glues decompose rapidly unless a preservative is used. Suitable products for this purpose are phenol, formic acid, benzoic acid, salicylic acid, benzaldehyde, Dowicide A, or Moldex.

Dextrin and gum arabic inhibit the gelatinization of glues and, at the same time, the glues improve the viscosity of dextrin and gum arabic solutions. Combinations of these adhesives are for these reasons frequently made.

The following formula represents the simplest type of liquid glue: ¹

Glue	100 gm.
Water	100-200 cc.
Acetic Acid	75-100 cc.

¹ Dulac, R. and Rosenbaum, J. L., p. 125, *Industrial Cold Adhesives*, Charles Griffin & Co., Ltd., London (1937).

The glue is soaked in water over night and is heated next day on a water bath to dissolve. The acetic acid is then added.

The following example illustrates the use of alum and acetic acid in a waterproof glue: ²

Potassium Alum	10 gm.
Acetic Acid	125 cc.
Glue	100 gm.
Alcohol, Denatured (95%)	125 cc.

Allow the glue to swell in the cold over night. Next day, heat it on the water bath for 5-6 hours to dissolve, replacing the acid as it evaporates. Add the denatured alcohol to the lukewarm solution.

Calcium chloride is used in the following formula to stabilize the liquid glue: ²

Glue	45.0 gm.
Water	55.0 cc.
Calcium Chloride (Anhydrous) ..	13.0 gm.
Phenol	0.5 gm.

The glue is soaked in water over night and dissolved the next day with gentle heating. The calcium chloride and phenol are then added and stirred until dissolved.

We discussed, above, the purpose of potassium bichromate and ammonium sulfocyanide in water resistant liquid glues and the following formulas illustrate their use: ^{3, 4}

Glue	100 gm.
Water	100 gm.
Glycerin	5 gm.
Potassium Bichromate	3 gm.

² Bennett, H., p. 18, Chemical Formulary, Vol. 5, Chemical Publishing Company (1940).

³ Same as 2, p. 21.

⁴ Same as 1, p. 127.

Soak the glue as usual and the next day heat gently to dissolve. When the solution is cold, add the potassium bichromate and stir until dissolved.

Water	200 cc.
Glue	100 gm.
Ammonium Sulfocyanide	5 gm.

Swell the glue in the water over night. Add the ammonium sulfocyanide and heat on a steam bath, with stirring, for 6-8 hours.

We have seen that urea is a useful solvent for casein. According to a patent it liquefies animal glues and produces a good carpenters' veneer glue as given in the formula below: ⁵

Glue	100 kg.
Water	200 kg.
Urea	8 kg.
Glycerin	8 kg.

Soak the gelatin in water and heat gently to dissolve. Add the urea and glycerin and stir until uniform.

Strong, stable, water resistant glues can be prepared from a mixture of glue and starch as directed in the following formula: ⁶

Starch	20 gm.
Sodium Naphthalene Sulfonate ...	10 gm.
Glue	80 gm.
Water	100 cc.
Formaldehyde	4 gm.
Sodium Bisulfite	2 gm.

⁵ German Patent 605,756.

⁶ Swiss Patent 192,582.

The glue is soaked in water over night. The next day, the glue is warmed on a water bath and stirred until dissolved. The starch is then mixed in and the mass is gently heated until completely gelatinized. The sodium naphthalene sulfonate is added next. When cold, add the formaldehyde and sodium bisulfite with rapid stirring.

Glues suitable for pasting labels on tin cans are difficult to formulate. The following mixture of gelatin, starch and sodium silicate is recommended for this purpose: ⁷

Wheat Starch	100 gm.
Water	700 cc.
Gelatin	10 gm.
Sodium Silicate	100 gm.
Turpentine	50 gm.

Mix the starch with 250 cc. water and heat the paste until completely gelatinized. Soak the gelatin in 450 cc. water over night and heat gently to dissolve. Mix the cold starch into the hot gelatin solution. When the paste starts to gelatinize, stir in the sodium silicate and when cold, mix in the turpentine.

Adhesives of glue and calcium sucate can be prepared in accordance with a formula given by Dulac: ⁴

Water	200.0 gm.
Calcium Hydroxide	30.0 gm.
Sugar	35.0 gm.
Glue	100.0 gm.
Phenol	0.1 gm.
Acetic Acid	0.7 gm.

The sugar, calcium hydroxide and 100 cc. water are heated to 80° for eight hours. The glue is soaked in 100 cc. water over night and heated the next day to dissolve. The calcium sucate and glue solutions are mixed while warm. Finally the phenol and acetic acid are stirred in.

⁷ Same as 2, p. 27.

CHAPTER IX

SODIUM SILICATE ADHESIVES

SODIUM silicate is an excellent adhesive for certain purposes. It is inexpensive, a strong and quick drying adhesive. It imparts stiffness to the articles on which it is used and in some cases this is an advantage. The chief difficulty in its general use is its strong alkaline reaction. It is generally applied to porous paper in the manufacture of corrugated paper and boxes. It dries by the absorption of its moisture by the paper to which it is applied. Although a strong adhesive, sodium silicate has little tack when wet. Pressure must be applied to the surfaces joined, to prevent them from flying apart, until the adhesive is dry. It is soluble in water and therefore not waterproof but the adhesive redissolves slowly when dry. Although bonds made with sodium silicate are weaker than those made with casein or animal glues, they are stronger than those produced with dextrin or starch pastes. Sodium silicate solutions are fire-resistant, do not become rancid, and are vermin-repellent.

There are many grades of sodium silicate, some of which are better suited to some applications than others. The various grades of silicate differ in their concentration and in composition. It was pointed out in Chapter III that sodium silicate is manufactured by the fusion of sand (SiO_2) and sodium oxide (Na_2O). The ratio of these components can be varied within wide limits. Naturally, the higher the caustic soda content, the more alkaline the silicate and the more likely it is to cause stains. However, the more alkaline silicates remain sticky longer and are more fluid

and mechanically more workable than those in which the sand or silica content is high. The proportions, in sodium silicate, of the lowest practical alkalinity are 1 part sodium oxide and 4 parts silica or as it is written in the trade $\text{Na}_2\text{O } 4\text{SiO}_2$.

The water resistance of certain cardboards depends on a rosin size applied on the surface. Highly alkaline silicates destroy this size rapidly. In this connection a surprising difference was demonstrated by Vail¹ between the action of silicates containing 9% Na_2O and 11% Na_2O . The cardboard made with the first silicate was much more water resistant than that made with the second. Vail's photographs on this subject are very instructive.

The type of silicate chosen must be adapted to the speed of the manufacturing operation. For boxes $\text{Na}_2\text{O } 3.3 \text{ SiO}_2$ is satisfactory but for wall board, where the operation is slower, $\text{Na}_2\text{O } 2.9 \text{ SiO}_2$ is recommended.¹ The danger of staining by silicates is increased when drying is slow. The alkaline component of the silicate seems to diffuse outward, leaving the silica in the interior. To avoid trouble, it is best to use a silicate with the lowest practical Na_2O content and to dry as rapidly as possible.

Sodium silicate is frequently mixed with other substances in the manufacture of adhesives. In some cases, the resulting product has the fused characteristics of its components but in other cases, where a chemical reaction sets in, the resulting product has properties different from any of the starting materials.

Excellent adhesives are prepared from a mixture of starch and sodium silicate. We have previously given an example of this type. Vail² gives the following formula:

¹ Vail, J. G., pp. 230-232, *Soluble Silicates in Industry*, Chemical Catalog Co. (1928).

² Same as 1, p. 244.

Starch	50 lb.
Water	100 lb.
Sodium Silicate	
(Na_2O 3.34 SiO_2) (sp.gr. 1.38) ...	50 lb.

The starch and water are stirred together and added to the silicate, and the mixture is stirred and heated on a steam bath until it is practically clear.

Dextrin is sometimes added to improve the tack of the silicate when wet, although the tensile strength suffers as a result.

The following is an adhesive of a similar nature. It is recommended for metal foils and is solvent resistant: ³

Wheat Starch	80 kg.
Water	550 kg.
Gelatin	8 kg.
Sodium Silicate (36–38° Bé)	80 kg.
Turpentine	40 kg.

Mix the starch with 200 kg. water and heat on a steam bath until the solution is clear. Soak the gelatin in 350 kg. cold water over night and on the next day *heat to dissolve*. Add the starch solution to the hot gelatin. Stir in the sodium silicate and when cold, add the turpentine.

By reaction with complex copper and zinc salts, modified silicates have been prepared.⁴

The following formulas were taken from the patent in which the adhesives are described as setting more rapidly and being more water resistant than the original silicate.

³ Bennett, H., Chemical Formulary, Vol. V, p. 20, Chemical Publishing Co. (1940).

⁴ Larson, L. L. to Grasselli Chemical Co., U. S. Patent 1,949,914 (1934).

Copper Sulfate	14.4 lb.
Water	16.5 lb.
Ammonium Hydroxide (sp.gr. 0.90) ..	14.9 lb.
Sodium Silicate	
(Na_2O 3.2 SiO_2) (42.5° Bé)	200.0 lb.
Water	14.6 lb.

The copper sulfate is dissolved in 16.5 lb. water and the concentrated ammonia is added. The deep blue solution is run into the sodium silicate slowly with constant stirring. The 14.6 lb. water is then added to reduce the viscosity to that of the original silicate solution.

This patent gives an additional formula calling for a larger amount of copper salt which, it is claimed, is even more water resistant.

In the following example, the patent covers more water resistant glues formed by adding soy bean meal and China wood oil.

(a) Soy Bean Meal	12.70 lb.
Water	22.30 lb.
Sodium Silicate	
(Na_2O 3.2 SiO_2) (38.5%)	65.00 lb.
(b) Sodium Silicate	
(same grade as above)	19.40 lb.
Wood Flour	5.10 lb.
Water	7.60 lb.
(c) Copper Sulfate	14.30 lb.
Ammonium Hydroxide	
(sp.gr. 0.90)	15.00 lb.
Water	41.30 lb.
(d) China Wood Oil (Blown)	13.10 lb.
Petroleum Sulfonic Acid,	
Sodium Salt	0.13 lb.

The ingredients in (a) are ground in a mill until thoroughly dispersed. (b) is added next with rapid stirring and is followed by (c). Finally (d) is added with thorough, rapid agitation.

The following zinc compound is a final example from this patent:

Zinc Sulfate (Heptahydrate)	10 lb.
Water	40 lb.
Ammonium Hydroxide (sp.g. 0.90)	15 lb.
Sodium Silicate	
(Na ₂ O 3.25 SiO ₂) (42.5° Bé)	200 lb.

The zinc sulfate is dissolved in 20 lb. water and the ammonium hydroxide is added to it. The clear solution is added to the sodium silicate diluted with 10 lb. water with rapid stirring and, finally, 10 lb. more water is added to reduce the viscosity to that of the original sodium silicate.

Lettig⁵ claims that paperhangers' starch paste can be improved by the addition of copper modified silicates. It is claimed that a paste, so modified, gives good results irrespective of the condition of the wall, provided it is clean. He prepares the modified silicate in accordance with the following formula:

Sodium Silicate	50 oz.
Water	44 oz.
Copper Sulfate (12.5% Solution) ...	6 oz.

The copper sulfate solution is run carefully into the diluted sodium silicate solution.

We have already seen in Chapter VI that valuable adhesives are obtained by modifying casein solutions with sodium silicate.

⁵ Lettig, G., U. S. Patent 2,005,900 (1935).

Gum arabic and gum shellac may be incorporated with sodium silicate with or without the addition of ammonia. According to Dulac⁶ a valuable modified silicate is obtained by incorporating rosin in the following manner:

Sodium Silicate (36° Bé)	100 lb.
Rosin	5 lb.

The rosin must be finely powdered and is added carefully to the sodium silicate, in a mixing pan fitted with a powerful agitator. The resulting product is described as being a pale, transparent solution which is more viscous, more adhesive, quicker drying, and less alkaline than the original silicate.

Blood albumin may be incorporated with sodium silicate in accordance with the following formula:²

Blood Albumin	45.0 lb.
Water	55.0 lb.
Sodium Silicate (Na_2O 2.9 SiO_2) ..	4.0 lb.
(sp.gr. 1.48)	

The ingredients are stirred until a homogeneous mass is obtained. Latex, stabilized with ammonia, may be incorporated with soluble silicates to produce softer and more flexible films.

Numerous silicate cements have been formulated, some of which have been patented. We can mention only a few here.

A cement for porcelain and metals is prepared as follows:⁷

⁶ Dulac, R. and Rosenbaum, J. L., *Industrial Cold Adhesives*, p. 142, Charles Griffin & Co., Ltd., London (1937).

⁷ Bennett, H., *Chemical Formulary*, Vol. V., p. 20, Chemical Publishing Co. (1940).

Calcium Fluoride (finely powdered)	2 lb.
Glass (powdered)	1 lb.
Sodium Silicate (36–38° Bé)	

Mix the powders into just enough sodium silicate to make a thick paste.

An acid proof cement for sealing stoppers in carboys is prepared in accordance with this formula: ⁸

Chalk or Silica	25.0 kg.
Alum	0.1 kg.
Sodium Silicate	75.0 kg.

Mix until uniform.

A strong adhesive for felt on metal was patented by Torri who uses emulsified asphalt: ⁹

Sodium Silicate	60 lb.
Emulsified Asphalt	12 lb.
Clay	28 lb.

The following waterproof cement was patented by McCullock: ¹⁰

Flint (powdered)	62 lb.
Sodium Silicate	14 lb.
Water	14 lb.
Aluminum Fluoride	10 lb.

Mix well and dry at 125°C. after application.

According to Vail, zinc and aluminum powders react

⁸ Same as 7, p. 33.

⁹ Torri, J. A. to J. W. Mortell Company, U. S. Patent 2,175,767 (1939).

¹⁰ McCullock, L. to Westinghouse Electric and Manufacturing Company, U. S. Patent 2,932,142 (1936).

sufficiently with sodium silicate (Na_2O 3.3 SiO_2) to attain a fair resistance to water in a few days.¹¹ Such cements when dry will take a polish and can be used for filling defects in castings.

Cement for Ceramics:

Lithopone	10
Powdered Quartz mix with Sodium Silicate to a thick dough	10

Iron Cement for High Temperatures:

Borax powdered is mixed and stirred	1
Zinc Oxide and	5
Pyrolusite are mixed with Sodium Silicate to a stiff dough	10

Cement for Marble and Alabaster:

Whiting are mixed and stirred with	100
Zinc Carbonate and	100
Sodium Silicate	50

¹¹ Same as 2, p. 202.

CHAPTER X

RUBBER DISPERSIONS AND SOLUTIONS AS ADHESIVES

RUBBER was first made use of by man long before the period of recorded history. It occurs in plants and trees that flourish in tropical climates. It flows in the form of a milky fluid from incisions made in the bark of rubber trees. In some cases, it is preserved with suitable chemicals, stabilized and shipped in this form as rubber latex. At other times, it is coagulated from the milky latex and formed into sheets or slabs and dried.

In this chapter, we are interested in rubber in the form of a water emulsion or latex.

The first practical process for redispersing coagulated rubber was developed by Pratt. He found that coagulated rubber can be brought into an emulsion if the coagulated rubber is kneaded in water containing a dispersing or emulsifying agent. This can be done with vulcanized, reclaimed and crude rubber.

By itself, latex is a weak adhesive. It is compounded with strong adhesives to impart elasticity to them. This can be done in numerous cases but not when the adhesive is strongly acid or alkaline or if the viscosity is too high.

For example two parts of the starch adhesive previously described can be mixed with one part latex to give a strong, elastic adhesive. Dulac ¹ says that this product is as elastic and flexible as latex alone and very much less expensive.

¹ Dulac, R. and Rosenbaum, J. L., p. 182, *Industrial Cold Adhesives*, Charles Griffin & Co., Ltd., London (1937).

The following formula illustrates the use of latex with casein: ²

(a) Bentonite	1.70 oz.
Water	10.30 oz.
(b) Ammonium Alginate	0.04 oz.
Water	0.96 oz.
(c) Casein	1.65 oz.
Ammonium Hydroxide (28%) ..	3.70 oz.
Zinc Oxide	0.05 oz.
Water	0.40 oz.
Ammonium Hydroxide (28%) ...	0.20 oz.
(d) Latex (38% Solids)	64.00 oz.
Accelerator	6.50 oz.

In (a) the bentonite and water are mixed together and added to the clear solution (b). The ammonium alginate acts as a suspending agent. In (c) the casein is dissolved in the mixture of ammonium hydroxide and water. The zinc oxide and excess ammonia are then added and the mixture combined with (a) and (b). The resulting mixture is stirred into (d).

Erdahl patented a solution of latex stabilized with ammonium alginate for the production of can joint seals: ³

Latex	60 oz.
Alginic Acid	40 oz.

The alginic acid is dissolved in ammonium hydroxide before it is added to the latex.

A gasket-like can seal may be formed with the following product: ⁴

² Canadian Patent 367,342.

³ Erdahl, B. F., U. S. Patent 2,013,651, (1935).

⁴ British Patent 441,877.

Colloidal Graphite (20% in water) ..	75 lb.
Gum Tragacanth ($\frac{1}{2}$ –1% Solution) ..	10 lb.
Latex (40% Solids)	22 gal.

McGowan and Preschin patented a mixture suitable for can paint gaskets: ⁵

Latex (40%)	28.0 lb.
Barytes	30.0 lb.
Casein	1.5 lb.
Sulfur	0.5 lb.
Diphenylguanidine	0.3 lb.
Zinc Oxide	4.0 lb.
Water	35.7 lb.

The casein is dissolved in a little ammonia before it is added to the other components. This mixture is particularly good because it expands on drying.

Wolff made an ingenious application of latex in a self sealing envelope adhesive in accordance with the following formula: ⁶

Latex (40–60%)	50 g.
Mica (powdered)	50 g.

The mica serves to anchor the latex to the paper.

The following formula gives a transparent adhesive for moisture proof “Cellophane”: ⁷

Latex (45% Rubber)	5 lb.
Water Soluble Agglutinant	15 lb.

⁵ McGowan, W. J. and Preschin, A. J., U. S. Patent 2,444,308, (1938).

⁶ Wolff, Ivan, U. S. Patent 2,093,105, (1937).

⁷ Charch, W. H.; Hyden, W. L.; Finzel, T. G., U. S. Patent 1,953,104, (1934).

Glycerin	3 lb.
Ethyl Lactate	5 lb.

The water soluble agglutinant is prepared by heating the following until a clear solution is obtained.

Water Soluble Agglutinant

Corn Starch	10 lb.
Dextrin	2 lb.
Water	63 lb.

A combination of glue and latex is used in the following formula to produce a waterproof cement: ⁸

Latex (40% Solids)	100 oz.
Water	45 oz.
Glue	10 oz.
Zinc Oxide	20 oz.
Sulfur	3 oz.
Titanium Dioxide	25 oz.
Potassium Bichromate	10 oz.

The glue is soaked in the water over night and the next day is heated to dissolve it. The glue solution is allowed to cool to room temperature before it is added to the latex. The other ingredients are added in the order mentioned.

An adhesive for metals involving the use of sodium silicate and latex can be prepared according to the following formula: ⁹

⁸ Bennett, H., p. 23, Chemical Formulary, Vol. IV, Chemical Publishing Company (1939).

⁹ Bennett, H., p. 8, Chemical Formulary, Vol. II, D. Van Nostrand Co. (1935).

Bentonite	20 lb.
Sodium Silicate (65%)	58 lb.
Latex (40%)	7 lb.
Water	15 lb.

Certain solvents, such as toluene, tend to swell rubber and make it tacky. Dulac¹⁰ utilizes this fact by making emulsions of latex and toluene with Turkey red oil. If desired, the adhesive can be strengthened by dissolving a resin in the toluene before emulsifying it. Different resins produce different degrees of adhesiveness.

Latex adhesives sometimes contain a vulcanizing ingredient which, after a baking process, hardens the adhesive layer.

¹⁰ Same as 1, p. 184.

CHAPTER XI

MISCELLANEOUS ADHESIVES

IN PREVIOUS chapters we discussed two classes of adhesives which are protein in nature, namely the casein and gelatin group. There are several smaller groups of a similar character, one of which is the albumin group. The white of egg or egg albumin is a common example of this type but its high cost makes it impractical for large scale industrial application. Blood is a much less expensive source of albumin and in fact, is sometimes used as is (with or without the red corpuscles removed) in adhesives. As a rule, however, the albumin is isolated by evaporation after the removal of the haemoglobin (red pigment). The outstanding difference between albumin and the other proteins is its property of being made insoluble merely by the application of heat. It resembles casein in that it forms a very insoluble product with calcium salts and that glues made in this manner have only a limited working life.

Where cost is not an important consideration, egg albumin may be used in accordance with the following formulas for bookbinders' size: ¹

Formula I

Egg Albumin	4-15 oz.
Water	35-70 oz.
Amyl Acetate	4-14 oz.

¹ United States Patent 2,089,063.

The amyl acetate serves to "denature" or insolubilize the albumin on drying.

Formula II

Egg Albumin	4-13 oz.
Glucose	3-10 oz.
Starch	1-5 oz.
Water	35-85 oz.
Acetic Acid (28%)	1-8 oz.
Ammonium Hydroxide (26%) ..	1-8 oz.

The starch is stirred into enough water to make a thin paste and is heated on a steam bath until a clear solution is obtained. The egg albumin is dissolved in the rest of the water and ammonium hydroxide. When the starch is cold, the glucose and egg albumin are added, with stirring, and finally the acetic acid is run in.

A simple lime albumin glue may be prepared with a mixture of calcium and ammonium hydroxide: ²

Lime-Albumin Glue

Blood Albumin	6.00 lb.
Water (at 27° C.)	11.00 lb.
Ammonium Hydroxide (sp. gr. 0.90) ..	0.25 lb.
Calcium Hydroxide	0.13 lb.

The water is poured over the blood albumin and allowed to stand undisturbed for at least two hours. The soaked albumin is stirred until it is in solution and the ammonium hydroxide is added, with slow stirring, to prevent foaming. The calcium hydroxide is then added and the suspension is

² Bennett, H., p. 32, *Chemical Formulary*, Vol. IV, Chemical Publishing Co. (1939).

stirred for a few minutes. The glue should have a moderate consistency and should be suitable for use for several hours. An excess of lime should be avoided as it turns the glue into a jelly.

The working life of an albumin glue may be increased by the addition of a silicate. In the following example, sodium fluosilicate is used for this purpose: ³

Blood Albumin	40 g.
Casein	12 g.
Calcium Hydroxide	6 g.
Sodium Fluosilicate	2 g.
Wood Meal	40 g.

The ingredients are mixed thoroughly in powder form and made into a paste with cold water just before using.

Blood albumin may be insolubilized with formaldehyde. To give the glue longer working life, a derivative of formaldehyde, paraformaldehyde, is used. Paraformaldehyde gives off formaldehyde slowly and as a result, the glue may be used for six to eight hours after it is prepared: ⁴

Blood Albumin (90% Solubility)	100.0 g.
Water	140.0–200.0 g.
Ammonium Hydroxide (sp. gr. 0.90) .	5.5 g.
Paraformaldehyde	15.0 g.

The blood albumin is soaked in water and the mixture is allowed to stand 1–2 hours and then stirred slowly. Ammonium hydroxide is added next with more stirring. The paraformaldehyde is then sifted in and the mixture is

³ Bennett, H., p. 5, Chemical Formulary, Vol. III, D. Van Nostrand Co. (1936).

⁴ Bennett, H., p. 8, Chemical Formulary, Vol. I, Chemical Publishing Co. (1933).

stirred quite rapidly. It should be added not so quickly that lumps form nor so slowly that the mixture thickens or coagulates before the required amount has been added. As this mixture thickens, it becomes difficult to stir. However, in a short time the mass becomes fluid again and assumes a good working consistency in about an hour.

Albumin is thermoplastic (it softens on moderate uniform heating) and as a result a dry mixture of sodium metasilicate and albumin may be used as an adhesive.⁵ A mixture of equal weights of albumin and sodium metasilicate is simply powdered on the surfaces to be joined. The plywood (or other material) is put into a press and heated a little above room temperature to set the glue.

During the last decade, soy bean protein has become a very important raw material for plastics. In some reactions it resembles casein and similar types of glues can be prepared with it. According to Hovarth⁶ the viscosity of concentrated soy protein solutions is far above that of casein. A soy protein solution can therefore be diluted more and is more economical to use. The equality of soy protein depends upon the method by which it was extracted from the soy bean meal and the process by which the soy bean oil was extracted from the meal.

In the U.S.S.R., the following formula was found satisfactory as a glue for airplane veneers.

Soy Protein	100 lb.
Calcium Oxide	15 lb.
Water	500 lb.
Sodium Silicate	7 lb.
Cement	2 lb.

⁵ Cleveland, T. K., Hill, Drexel, Stericker, W. to Philadelphia Quartz Co., U. S. Patent 2,044,466, (1936).

⁶ Hovarth, A. A., p. 187, *The Soybean Industry*, Chemical Publishing Company (1938).

The lime (calcium oxide) is slaked with a little of the water. The rest of the water and the soy protein are stirred in. This is followed by the silicate and cement.

A simpler formula for a soy glue is given below: ⁴

Soybean Flour	100 lb.
Calcium Hydroxide	10-20 lb.
Sodium Hydroxide	5 lb.
Water	100 lb.

Another variation of this type of glue is the following formula: ⁷

(a) Soybean Flour	18.0 kg.
Soda Ash	0.8 kg.
Water	81.2 kg.
(b) Calcium Oxide	10.0 kg.
Water	50.0 kg.
(c) Soda Ash	4.0 kg.
Water	10.0 kg.
(d) Sodium Silicate	30.0 kg.
(e) Carbon Bisulfide	1.8 kg.
(f) Carbon Tetrachloride	1.2 kg.

The solutions are made up individually and mixed in the order given above.

Satow compounded a waterproof glue suitable for the manufacture of veneers. He uses both lime and formaldehyde to insolubilize the glue as given in the following formula: ⁸

Soybean Flour (Oil free)	100.0 oz.
Disodium Phosphate	10.0 oz.

⁷ Italian Patent 352,378.

⁸ Satow, Teikichi, U. S. Patent 1,994,050, (1930).

Sodium Fluoride	5.0 oz.
Calcium Hydroxide	7-10.0 oz.
Calcium Carbonate	50.0 oz.
Copper Sulfate	0.5 oz.
Sodium Chloride	2.0 oz.
Water	530.0 oz.

All of the dry ingredients are mixed in powder form and stirred into the water before use. To insolubilize the glue he adds 5-10 oz. of the following reaction product:

Formaldehyde	35 oz.
Ammonium Hydroxide (18%)	105 oz.

The ammonium hydroxide is added slowly to the formaldehyde so as to maintain the temperature between 15-20°C. during the addition. This glue remains fluid 6-10 hours and is completely set in twenty-four hours.

Rosin or colophony is a plentiful and inexpensive raw material. It is the residue left in the still after the removal of the turpentine from pine balsam. It appears on the market in many qualities, classified largely on the basis of color, the lightest colored being the most expensive.

Rosin is soluble in a number of different solvents and finds use as an adhesive in solvent solution. This will be discussed in the second volume on water insoluble adhesives. Chemically, rosin consists largely of an acid called abietic acid. Rosin combines with alkalis to form rosin soaps which give sticky solutions. They can be made in highly concentrated form which set and dry quickly. This type of adhesive is largely used on paper because it is so inexpensive and tacky. It is frequently used in combination with other types because it imparts improved tack and stability to the mixture. However, it is very soluble in

water and should not be used where water resistance is of any importance.

As a rule, rosin soap is formed by adding a solution of sodium hydroxide or soda ash to the molten rosin. Generally, the amount of alkali added is not enough to react with all of the abietic acid of the rosin. The excess rosin remains suspended in the rosin soap which is an efficient emulsifying agent for some purposes. A stable rosin emulsion which is more sticky than the pine rosin soap, is obtained if 10–15 per cent of the rosin is left unreacted: ⁹

The following formulas are simple examples of rosin adhesives:

Sodium Resinate Adhesive ¹⁰

Rosin	100.00 lb.
Water	80.00 lb.
Sodium Hydroxide	11.25 lb.

The rosin is melted and the hot solution of the alkali is run in with active stirring.

Potassium Resinate Adhesive

Rosin	100.00 lb.
Water	80.00 lb.
Potassium Hydroxide	14.65 lb.

There are times when a sticky, non-drying adhesive is required. The following formula gives a product of this type: ¹⁰

⁹ Dulac, R. and Rosenbaum, J. L., p. 138, *Industrial Cold Adhesives*, Charles Griffin & Co., Ltd., London (1937).

¹⁰ Bennett, H., p. 43, *Chemical Formulary*, Vol. V, Chemical Publishing Co. (1940).

Non-drying Adhesives

Rosin	60.0 oz.
Diethylene Glycol	14.0 oz.
Potassium Hydroxide (40%)	7.5 oz.
Yumidol (83% Sorbitol)	9.0 oz.

The rosin is dissolved in the diethylene glycol with heat. The potassium hydroxide and Yumidol are then added and the mass is stirred until uniform.

Rosin darkens with age when exposed to light. When color is important, "Staybelite A" may be used. This product has the reactions of rosin but, as its name implies, is unaffected by light. Where color is not a consideration, the dark but inexpensive "Vinsol" resin may be considered to replace rosin.

An alcoholic solution of rosin has been combined with an aqueous solution of gum arabic and invert sugar to produce an adhesive for waxed paper.

Sulfite liquor is a by-product from the manufacture of wood pulp. Its use in adhesives has been extensively investigated and has been the subject of a number of patents. Sulfite liquor produces a flexible film and is very inexpensive but it is acid, dark in color, hygroscopic and a rather poor adhesive. It is used alone with calcium compounds or in combination with other adhesives as the following examples illustrate: ³

Sulfite Lye (33° Bé)	100.00 lb.
Calcium Hydroxide	11.00 lb.
Water	80.00 lb.

The calcium hydroxide is mixed with water and added to the sulfite lye. The mass is stirred and heated for one hour.

Sulfite Lye (33° Bé)	100.0 lb.
Calcium Hydroxide	2.6 lb.
Water	90.0 lb.
Sodium Carbonate	2.0 lb.
Casein	10.0 lb.

Soak the casein in 70 lb. warm water. Add the sodium carbonate and stir the mass until the casein is in solution. Add 0.6 g. calcium hydroxide and stir until uniform.

Neutralize the sulfite liquor with about 2 lb. calcium hydroxide suspended in 20 lb. water. When the solution is neutral to litmus, combine it with the casein solution.

Sulfite Lye (33° Bé)	100.0 lb.
Lead Acetate	5.3 lb.
Gelatin (glue)	10.0 lb.
Water	10.0 lb.

Soak the gelatin in the water and when swollen add to the sulfite liquor. Mix and boil until mass is homogeneous.

Ethyl silicate has been available in commercial quantities for some years. It deposits silica on decomposition with water, and is useful as a binding agent for waterproof and acidproof cements where the high cost is not a factor.

Polyvinyl alcohol is a relatively new product which is soluble or dispersible in water. It is of interest in adhesives because of its freedom from color, odor and taste. It is not attacked by bacteria and produces strong films which impart toughness and flexibility to glues. It blends readily with other adhesives such as rubber latex, starch, casein and soy protein. Some grades may be used as adhesives of the remoistable type. The adhesives made from it do not stick in high humidities.

Polyvinyl alcohol may be used as a thickening agent in adhesives. To prepare a water solution, stir the powder in

cold water (20°C. or lower) until all the lumps are broken up and the mixture is smooth. This is now heated on a steam bath, with stirring, until a clear solution is obtained.

The following is an interesting example of a special type of adhesive that may be prepared with polyvinyl alcohol: ¹¹

Starch	25-30 g.
Polyvinyl Alcohol (RH-349)	
(3%-4% solution)	100 g.

The starch is merely stirred into the polyvinyl alcohol solution until a smooth suspension is obtained.

If this composition is used, for example, in sticking paper to paper, the adhesive is almost instantaneously set by the application of moderate heat to the cemented area. This is due to the rapid absorption of the water in the mixture by the uncooked starch granules when heat is applied.

During the past few years a water soluble cellulose derivative was put on the market in this country. It is called methyl cellulose and is produced in several grades depending upon the viscosity of its solution in water. It is odorless and colorless and not subject to attack by bacteria. It is useful in thickening aqueous dispersions of casein, starch and other adhesives. The high toughness and flexibility of the methyl cellulose films strengthen and flexibilize the adhesive layer. Methyl cellulose adheres to paper strongly when applied in water solution. This film is greaseproof and is useful in applying liners to paperboard where greaseproofness is required. For an adhesive of this kind, the methyl cellulose may be used alone or in combination with 10-20% gelatin.

Alginic acid or sodium alginate (as mentioned previously) is a thickening agent derived from certain marine

¹¹ Polyvinyl Alcohol. Technical Bulletin, E. I. du Pont de Nemours & Co.

plants called algae. Since the development of methyl cellulose there seems to be little reason to use the alginates in many cases since they do not offer all the advantages of methyl cellulose and have several disadvantages. The commercial alginates are not altogether colorless or odorless and are readily decomposed by bacteria. They are insoluble in acid solution and gradually break down in strongly alkaline solution. A soluble alginate is precipitated by calcium salts and therefore cannot be used in many adhesives.

Pectin is another natural product that has a limited application in adhesives. It is derived from certain fruits, particularly apples and citrous fruits and is useful as a thickening agent. The following formula illustrates its uses: ¹⁰

Pectin	50 oz.
Bone Glue	10 oz.
Dextrin	10 oz.
Rye Flour	5 oz.

Dissolve in boiling water.

Other Reference:

German Patent 421,682, (1924).

PLYWOOD ADHESIVES

Adhesive	Source	Form Supplied	Cold or Hot Press	Added Ingredients of Mix	Preparation for Use
Blood albumen	Dried beef blood	Powder, flake	Hot press	Water, alkalis, paraformaldehyde, corn syrup, invert sugar, hydrated lime, albuminous adhesives, etc.	Mixed cold
Casein	Precipitated from milk	Powder	Mainly cold; some hot	Water, CH_2O , preservatives, and alkalis (lime and sodium salt)	Mixed cold
Animal Glue	Hides and bones of animals cooked in water, evaporated, jellied, dried	Powder, pearl flake, shreds	Cold, and cold with warm cauls	Water, some preservatives	Soaked in cold or warm water, followed by cooking
Vegetable starch	Vegetable carbohydrate, base mainly cassava (tapioca); also potato flour	Flour	Cold	Water and alkalis (sodium hydroxide)	Generally mixed hot
Soya Bean and vegetable protein	Mainly soya bean meal; also peanut and cottonseed meal	Flour	Mainly cold; some hot	Water, lime, silicate of soda, carbon bisulfide	Mixed cold with water
Urea-formaldehyde resins	Urea- CH_2O condensation	Powder and liquid	Mainly hot; some cold	Water, accelerators, vit. at and rye flours	Some mixed with water only; others accelerator and flour added
Phenol-formaldehyde resins	Phenol- CH_2O condensation	Lumps, powder, liquid and film	Mainly hot; some cold	Alcohol and water, flour fillers	Dry film as is. Liquid resin as is. Solid resin dissolved in alcohol and water. Catalyst added for cold pressing. Warm setting, and fast hot pressing.
Thermoplastic resins	Chiefly plasticized polyvinyl butyraldehyde	Resin solution in organic solvent	Hot press	None, thin with solvent if necessary	None
Blood and urea-formaldehyde combined	Urea resin plus dried blood	Resin and blood separately	Hot press	Water, accelerators, wheat and rye flours	Mix ingredients cold
Blood and phenol-formaldehyde combined	Phenol resin plus dried blood	Resin and blood supplied separately or mixed	Hot press	Water and reagents	Mix cold or use as supplied

Life of Mixture	Spreading and Handling Equipment	Spread (ft./lb.) Dry Basis	Assembly Time in Minutes	Pressing Temp.	Pressing Time	Moisture Content Allowed in Veneers
2 hours to several days	Roller spreader	30-100	10-40	180-250° F.	3 min. for hot press; varies with thickness of panel. Overnight cold press	2-3% for faces; 5% or less for cores and crossbands
2 hours to 2 days (preferably hot)	Roller spreader	30-80 Medium mixture	1-20	Ordinary room temp. for cold press. 180-250° F. hot press	2-18 hrs. for cold press. 3 min. for thin panels hot press	Same as above
Extended, if preserved	Heater, roller spreader	30-40	1-15	Cold with warm cauls	2-18 hr.	Same as above
Many days	Roller spreader	30-50	1-40	Ordinary room temp.	4-18 hr.	Same as above
Several hours for cold process	Roller spreader	27-40	1-20	Cold at room temp. Hot press at 180-250° F.	2-5 hr.	Same as above
Several hours to 1 day	Roller spreader	40-60	1-60	210-240° F.	3 min. for thin panels hot press. 8 hr. for cold pressed	2-15%
Extended period for hot press material. Several hours for cold press resin	Liquids in roller spreader. Film used as is.	25-40 for cold press resin. 70-100 for hot press liquid. 80-90 for film	Hot press liquid: 10 min. to sev. wks.; film: sev. months. Cold press; 5-30 min.	220-230° F.	6 min. for thin panels hot press; overnight for cold press	3-14% for liquid resin. For film, cores and crossbands: 5-10%. Faces: 2-6%
Indefinite hot active	Roller spreader	6-12	Several hours plus—must be dried	230-300° F.	Few minutes to several hours—must be cooled in press or mold	3-12%
Several hours	Roller spreader	40-80	1-20	220-260° F.	3-8 min.	5-15%
Hot—toasting	Roller spreader	40-80	1-20	220-250° F.	3-8 min.	3-8%

PLYWOOD ADHESIVES—Continued

Adhesive	Conditioning of Panels After Pressing	Dry Bond Strength	Wet Bond Strength	Water Resistance	Mold Resistance	Staining Power	Heat and Fire Resistance
Blood albumen	Unnecessary for hot press; necessary for cold press. Dry to: 7% M.C. for indoors 12% M.C. for outdoors	Medium	Medium	Medium	Poor to good	Low to high	Poor
Casein	Same as above	Medium	Poor to medium	Poor to good	Generally poor	Generally marked	Poor
Animal Glue	Same as above	Very high	None	Poor	Poor	Some staining	Poor
Vegetable starch	Same as above	Medium	None	Poor	Poor	Generally marked	Poor
Soya Bean and vegetable protein	Same as above	Medium	Poor to medium	Fair	Poor	Marked	Poor
Urea-formaldehyde resins	None	High	Medium to high	Cold water: Good. Hot water: Poor	High	None	Moderate
Phenol-formaldehyde resins	Generally none, sometimes dipped or sprayed with water	Medium to high	Excellent in both hot and cold water	Excellent	Excellent	Some staining with liquids; none with film	High
Thermoplastic resins	Generally none, sometimes sprayed	Low to medium	Medium	Medium	High—not affected	None	Poor
Blood and urea-formaldehyde combined	None usually	High	Medium	Good	Uncertain	No stain. May diffuse	Moderate
Blood and phenol-formaldehyde combined	None	High	Medium	Good	Uncertain	No stain. May diffuse	Moderate

Moisture Transmission	Exterior Durability	Relative Cost	Principal Uses	Special Features
Marked	Fair to good	Medium to high	Refrigerator, truck and car panels; special panels; packaging	Especially suitable for low temp. hot pressing; most durable of adhesives except resins. Also mixed with casein and soya bean flours.
Marked	Poor	Medium to high	Furniture and interior panels, concrete forms	Superior to vegetable glue for wet strength.
Marked	None	High	Principally for lumber cores and joints	Relatively expensive. Easy to use.
Marked	None	Very low	Furniture panels, games, production work, packages	Inexpensive, popular adhesive. Most eastern plywood made with cassava flour.
Marked	Poor	Very low	Douglas fir panels, building boards; concrete forms	Mostly soya bean meal used on Douglas fir.
Medium	Good	Resin alone: high. With fillers: low	Wall panels; radio cabinets; furniture; boats and aircraft	Very economical when mixed with flour. Provides a highly water resistant bond set hot or cold.
Low	Excellent	High	Two-ply facing; exterior panels; aircraft skins; boats	By far the most durable bond; resists all forms of deterioration.
Low	Poor to good, depending on conditions	High	Molded plywood	Flows at elevated temperature. Must be cooled in press. Will reseat. Plies retain flexibility.
Medium	Good	Medium	Panel stock, furniture	Rather critical to handle. Partially resistant to boiling water.
Medium	Good	Medium	Douglas fir	Popular for Douglas fir because good durability is attained with fast low temperature cycle.

CHAPTER XII

EQUIPMENT FOR THE MANUFACTURE OF ADHESIVES

IN PLANNING the location of an adhesive factory, one must first of all be assured of an ample supply of soft water. Hard water or a supply that is not carefully controlled and which varies widely in composition can be the source of endless difficulties. Having brought good water to the plant, the next problem is to keep it in condition within the factory itself. The pipes should be of the best grade of wrought iron and if the cost of the initial installation is not a vital consideration, brass pipe may be used to advantage for the smaller sizes. Savings in maintenance more than compensate for the additional cost of the best materials used.

In planning pipe layouts, one should guard against low spots where water or steam condensate may collect. Even the best wrought iron will rust under some conditions. In some plants, live steam is blown directly into the batch and in such cases steam lines should be blown out thoroughly before they are used. Rust, whether from the water or steam, can discolor and spoil many a batch.

Care should be exercised in the choosing of the materials from which the units are to be constructed. Wooden tubs, especially those built of Gulf Cypress, give many years of service even under adverse conditions. Circular tubs can be washed and steamed out thoroughly, but in some cases that may not be enough as wood is absorbent and a batch may be contaminated by small residues from the preceding

batch. In such cases it is necessary to use metal or enameled or glass lined tanks.

Heating a batch in a wooden tub offers some difficulties. The simplest solution is to blow live steam into the batch. This can be done only if the volume of water used in the batch is large enough so that adjustments can be made for the water formed from the condensed steam. Heating coils can be installed in wooden tubs but they are not entirely satisfactory as a rule. Wood is a good heat insulator and as a result a batch cools down much more slowly in a wooden tub than in a metal tank. This is a distinct disadvantage when a batch must be stirred until cold since it wastes power and reduces production.

Jacketed kettles are satisfactory for the manufacture of most adhesives. Batches are heated by steam passed through the jacket. In this way, formulas can be carefully reproduced especially if the kettle is closed and evaporation is reduced to a minimum.

In most cases, iron or ordinary steel kettles are not entirely satisfactory if the adhesive contains a high proportion of water. If initial cost is not of paramount importance stainless steel, copper, brass, enameled or glass lined kettles are more desirable. In most cases, due to the high alkalinity of the adhesive, aluminum or enameled equipment may not be used. Adhesives that contain a high proportion of concentrated sodium silicate can be prepared in ordinary iron kettles since the silicate forms a good protective coating. It should be borne in mind when working with latex, that minute amounts of copper have a bad effect on the ageing of rubber.

Agitation is an important factor in making adhesives. The type of mixing equipment must be chosen with the viscosity of the adhesive and the size of the batch in mind. For very viscous masses, the kneading type of agitator is used. In small lots where mixing is carried out in the cold,

a pony mixer, in which the blades rotate off center in one direction and the can in the opposite direction, is highly effective for paste products.

For fluid products, removable agitators of the propeller type are useful. These mixers can be obtained in various sizes which operate at different speeds. Blade type agitators operated by gears may also be used on adhesives of moderate viscosity.

In some processes, large changes in viscosity occur in the various stages of manufacture. For this reason it is necessary to purchase mixers that run at more than one speed.

For small plants, the temperature can be controlled with an ordinary thermometer. For complex processes, it is best to have mechanical recording thermometers so that responsibility can be fixed if batches go wrong.

Wherever possible, the layout of the factory should take advantage of gravity flow. Pumping corrosive or viscous liquids is both expensive and difficult. Kettles are best emptied through large gate valves in the bottom. The whole batch can be emptied in this way without any loss in the kettle and the unit can be cleaned out thoroughly.

CHAPTER XIII

WATER INSOLUBLE ADHESIVES

THE VARIOUS types of water soluble adhesives have already been discussed. At this point we shall consider the water insoluble adhesives. Some of the raw materials are the same in both classes, the difference lying in the manner in which they are used. In some cases this results in an unavoidably arbitrary division. For example, in the case of rubber it is necessary to consider some aspects of the water dispersed and the solvent types together in order to bring out the differences involved.

We shall limit our consideration of cements to such products as are used for joining two surfaces. Generally the relative proportion of the adhesive is small. We shall not consider those cements, asphalts, etc. that are used in huge quantities for building or road construction.

Many of the water insoluble adhesives have been developed in recent years. Their composition and manufacture are very complex. In some cases, the use of some chemical terms will be unavoidable but the discussion will be made as simple as possible and no chemical knowledge will be presupposed.

CHAPTER XIV

RUBBER ADHESIVES

RUBBER is principally obtained as a milky exudation (latex) from the rubber tree. This milky liquid contains, in addition to rubber, a small amount of several different proteins. For many applications, the presence of these proteins does no harm. Recently it has been found that the proteins make rubber less waterproof. This has led to the development of deproteinized rubber.

Rubber is soluble in benzol, petroleum ether, carbon bisulfide, carbon tetrachloride, chloroform, turpentine and other solvents. Only the first three mentioned are used commercially for the manufacture of rubber cements. When rubber is put in contact with its solvents, it first swells slowly, and forms a jelly-like mass and then, if enough solvent is added, goes into solution. These rubber solutions are very viscous. About 12% rubber is the maximum practical concentration.

In contrast to this, we find that in latex (a natural emulsion of rubber in water) the rubber concentrations can be as high as 60%. These highly concentrated latices are obtained from natural latex which contains about 40% rubber, in one of several ways. In one process, the latex is concentrated by evaporation in the presence of potassium hydroxide, a potassium soap or some other stabilizing agent. The product is of a creamy consistency and contains about 75% total solids of which 7-8% consists of the protein serum solids and added stabilizing substances. Another process consists of concentrating the latex by centrifuging it. In this way a thin creamy liquid is obtained. It retains

only a small portion of the protein substances present in the original latex and contains about 60 per cent rubber. In a third process, a solution of gum tragacanth or ammonium alginate is added to the latex. Two layers are formed, the upper layer, a creamy fluid, contains most of the rubber at a concentration of about 58–62 per cent.

Latex emulsions are frequently stabilized by the addition of ammonium hydroxide. In some cases, where the ammonia odor is objectionable, the latex is neutralized. This destabilizes the latex causing it to set and dry more readily than would otherwise be the case.

Rubber exists in latex in the form of minute particles, some of which are so small, that they cannot be seen, even under a powerful microscope. If a water emulsion of oils, resin or solvent is added, the two emulsions exist independently of each other and there is no action of the solvent or other substance on the rubber. When the purpose is to soften or plasticize the rubber with some material, it is necessary to destabilize the latex rubber, in some way, so that the softening compound may act on the rubber; either while both are in suspension or when the film is dry. This destabilization may be effected in various ways, for example by alcohol or heat. Certain drying oils modify the physical characteristics of rubber without coagulation and in such cases destabilization is unnecessary.

The adhesive properties of latex can be improved by the addition of certain substances which improve the tack. Vegetable and mineral oils, resins, gelatin and casein are examples of such materials. We have seen a number of formulas of this kind in previous chapters. The tack can also be improved by special treatment as by heating the latex for several hours, in the presence of a modifying agent such as mercaptobenzothiazol.¹

¹ Noble, R. J., p. 324, *Latex in Industry*, The Rubber Age, New York (1936).

Rubber cements are prepared by masticating rubber in the presence of a solvent. This process reduces the strength of the rubber film. The ageing qualities of a film produced from a solvent are much poorer than those of a film derived from latex. Because of their high viscosity, rubber solutions do not spread as well as latex cements. A 38 per cent latex cement will cover four or five times as much area as a 12 per cent solvent cement. Other shortcomings of rubber solvent cements are that the solvents are highly objectionable because of odor, toxicity or inflammability. Solvent cements, however, are not without advantages. A rubber solution dries rapidly and has such high tack in a few minutes that the surfaces to be joined can be left alone, shortly after pressing them together. On the other hand, a latex film is not tacky until dry and this generally takes about fifteen minutes. Premature pressure may coagulate the rubber and then it loses its adhesive power, unless the pressure is continued or repeated when dry. As the latex film dries completely, it quickly loses its tackiness; thus, the pressure must be applied just at the right time.²

When applied to fibrous surfaces, latex cements penetrate better and give a better bond. However, latex cements do not adhere well to vulcanized rubber but do adhere to uncured rubber. In the boot and shoe industry, rubber soles are attached to leather shoes by applying a latex cement to the leather and a solvent cement to the rubber sole. The two cements bond with each other, firmly. A cement containing rubber both in solution and in latex form can be made. A similar situation exists in metal to rubber adhesions. Two fluids need not be used but a compound metal to rubber cement may be prepared.¹

² Flint, C. F., p. 597, *The Chemistry and Technology of Rubber Latex*. Chapman & Hall, Ltd., London (1938).

Cement for Rubber to Metal

Rubber Cement (12% Rubber in Benzol)	100.00 gm.
Latex	5.00 gm.
Zinc Oxide	0.12 gm.
Sulfur	2.40 gm.
Accelerator	0.12 gm.

Strong, flexible adhesives are required for the manufacture of leather belts for power drives. Such products are frequently based on rubber, rosin and linseed oil.

*Cement for Leather Driving Belts**(Formula I)*

Rosin (Light)	30 gm.
Rubber (Dry, Waste)	20 gm.
Linseed Oil Varnish	20 gm.
Benzine (High Boiling)	30 gm.

Heat the rosin, rubber and linseed oil together until completely dissolved. Add the benzene, taking precautions against fire.

(Formula II)

Rubber (Raw)	10 gm.
Rosin (Powdered)	20 gm.
Linseed Oil	20 gm.

Heat together and stir until homogeneous.

The following formulas are examples of solvent cements modified by the addition of certain natural gums.

*Brown Cement*³

Rubber (Gum)	10 gm.
Carbon Bisulfide	100 gm.
Shellac (Powdered)	2 gm.
Alcohol	8 gm.

Dissolve the rubber in the carbon bisulfide. Add the alcohol, slowly with stirring, avoiding clots. Add the powdered shellac and heat on a boiling water bath until all the shellac is dissolved and the carbon bisulfide is driven off.

*Rubber Cement for Glass*⁴*(Formula I)*

Rubber	1 gm.
Mastic Gum	12 gm.
Dammar Gum	4 gm.
Chloroform	50 gm.
Benzene	10 gm.

Dissolve in the cold.

(Formula II)

Rubber	2 gm.
Mastic Gum	6 gm.
Chloroform	100 gm.

Dissolve in the cold.

³ Standage, H. C., p. 11, *Cements, Pastes, Glues and Gums*, Eighth Impression, C. Lockwood & Son Ltd., London (1931).

⁴ Same as 3, p. 39.

*Hard Cement for Crockery*⁵

Rubber	1 oz.
Shellac	1 oz.

Melt together on a boiling water bath.

The following formulas involve the use of latex and supplement the ones presented in previous chapters.

Insole Cement

Latex (40% Solids)	100 lb.
Casein Solution (10%)	10-15 lb.
Resin Emulsion (50%)	10 lb.

The casein solution is prepared as follows:

Casein	5 lb.
Water	44 lb.
Ammonium Hydroxide	8 oz.
Phenol	1 oz.

The following directions are used in the preparation of the resin emulsion:

Resin (Ester, Gum, or Cumar)	3 lb.
Oleic Acid	3 oz.
Ammonium Hydroxide	1 oz.
Water	3 lb.

The oleic acid and ammonium hydroxide are dissolved in the water and the resin is emulsified by heating to the melting point and stirring vigorously.

⁵ Same as 3, p. 40.

*Masking Tape*⁶

Rubber (Neutral Latex 70%)	100 gm.
Castor Oil	50 gm.
Rosin	5 gm.

The rosin is heated in the castor oil, until it is dissolved. The solution is then added to the latex.

CHLORINATED RUBBER

Rubber reacts with chlorine to produce a substance which finds some application in adhesives but has its greatest use in protective coatings. Chlorinated rubber is manufactured from rubber and should not be confused with chlorine containing rubber-like products which are entirely synthetic. The two materials have entirely different properties. Chlorinated rubber is insoluble in water, petroleum solvents and alcohols. It is soluble in benzene and other coal tar solvents, chlorinated solvents such as ethylene dichloride and in various ester solvents. It is sold in a number of viscosity grades. By itself, the film is brittle but it can be compounded to almost any degree of flexibility with castor oil, coumarone and indene resins, and some of the natural resins such as gum elemi. Its outstanding properties are that it is unaffected by acids and alkalis and many other chemicals. It is stable, non-inflammable and thermoplastic. It should find application in acid and alkali-proof adhesives of the solution type. There are chlorine derivatives of an entirely different type that find some use as thermoplastic adhesives. These are the chlorinated diphenyls which are offered in a number of grades ranging from light yellow oily liquids to yellow transparent sticky resins.

⁶ Same as 1, p. 329.

CHAPTER XV

ROSIN AND ITS DERIVATIVES

ROSIN is obtained from the liquid that flows from certain varieties of pine and fir trees. It is sold in a number of grades depending upon the color and melting point. Although quite soft and brittle it breaks with a glassy fracture. It softens at 80° C. and different qualities melt at temperatures between 100° and 135°C. As we have already seen, rosin reacts with alkalis to form soaps.

Rosin is too brittle to be used as an adhesive alone. Castor oil is a good and inexpensive plasticizer for it and the proportions used may be varied depending upon the type of adhesive desired. If a large amount of castor oil is used, the adhesive does not set and remains sticky. At lower proportions of castor oil, the adhesive sets when cold and it either must be melted for use or dissolved in a solvent:

*Rosin Adhesive Solution*¹

Castor Oil	17 lb.
Rosin	100 lb.
Alcohol (Denatured)	50 lb.

The rosin and castor oil are heated together until a homogeneous liquid is obtained. The denatured alcohol is then added and the mixture is heated until the solution is clear. The rate of drying or setting of a rosin solution ad-

¹ Dulac, R. and Rosenbaum, J. L., p. 158, *Industrial Cold Adhesives*, Charles Griffin & Co., Ltd., London (1937).

hesive may be modified by the choice of solvents. Besides being soluble in alcohol, rosin dissolves in methanol, amyl alcohol, acetone, ether, chloroform, turpentine, benzene and other solvents.

Sticky compositions for fly paper may be made from mixtures of rubber and rosin:

*Sticky Rubber-Rosin Adhesive*¹

Benzene	60 lb.
Rosin	100 lb.
Castor Oil	3 lb.
Crepe Rubber	5 lb.

Dissolve the rosin in the benzene, with heat, and add the rubber. When it is all dissolved, add the castor oil. If the adhesive is wanted in paste form, whiting or precipitated chalk may be stirred in.

Rosin-castor oil adhesives can be modified by the addition of bentonite. The adhesive obtained in this way is described as being opaque, creamy, ropy, very sticky and inexpensive. It is recommended for use on flexible materials, linoleum, rubber floorings and automobile upholstery. The paste is so viscous that it will not penetrate and stain fabrics.

*Rosin Linoleum Cement*²

(a) Castor Oil	5.0 lb.
Rosin	100.0 lb.
Bentonite (Refined)	10.0 lb.
(b) Bentonite (Refined)	2.5 lb.
Alcohol (Denatured)	75.0 lb.
Water	25.0 lb.

² Same as 1, p. 161.

The castor oil and rosin are melted together and the bentonite is stirred in. The mass is then permitted to cool to 75°–80°C.

The bentonite and alcohol are mixed and then the water is stirred in. The mass is heated to 75–80°C. and added to the rosin solution previously prepared. This paste is very viscous and requires a strong agitator. It should be stirred until cold.

Rosin may be compounded with numerous gums and resins to produce adhesives with various characteristics. We shall mention only a few typical examples. Such adhesives can be developed only by the trial and error method.

Paper or Celluloid to Metal Glue

Rosin	33 gm.
Camphor	2 gm.
Alcohol	65 gm.

*Glue for Bags*³

Rubber	6 lb.
Trichlorethylene	30 lb.
Rosin	10–15 lb.
Alcohol	42 lb.

Dissolve the rubber in the trichlorethylene and the rosin in the alcohol. Mix the clear solutions together.

*Paper to Metal Cement*⁴

Rosin	60 gm.
Mastic gum	10 gm.

³ H. Bennett, *Chemical Formulary*, Vol. 5, p. 19, Chemical Publishing Co. (1940).

⁴ Same as 3, p. 18.

Sandarac Gum	20 gm.
Ether	5 gm.
Alcohol	75-100 gm.
Dissolve in the cold.	

*Envelope Adhesive*⁵

Rosin	320 gm.
Mastic Gum	60 gm.
Sandarac gum	100 gm.
Ether	100 gm.
Alcohol	100 gm.
Dissolve in the cold.	

Rosin forms a water insoluble soap with calcium hydroxide which may be used as an adhesive when properly plasticized.

*Electrical Sealing Compound*⁶

Rosin	200 lb.
Calcium Hydroxide	10 lb.
Methyl Abietate	12 lb.

Melt the rosin by heating it to above its melting point. Stir in the calcium hydroxide and maintain the heat for 20 minutes. Stir in the methyl abietate at 150°C.

In another example, rosin is compounded with asphalt and rubber.

⁵ Bennett, H., p. 17, *Chemical Formulary*, Vol. V, Chemical Publishing Co. (1940).

⁶ United States Patent 2,075,885.

*Thermoplastic Sealing Cement*⁷

Rosin	150 gm.
Asphalt	25 gm.
Rubber	75 gm.
Turpentine	25 cc.

The rosin and asphalt are melted together. The rubber is added, a little at a time. The mass froths a great deal and, when it is homogeneous, the turpentine is added.

Chemically, rosin is largely abietic anhydride which is closely related to abietic acid. It combines with glycerin, glycols and various alcohols. With glycerin, a technically important rosin is produced. This product, called ester gum, is harder and less brittle than rosin. In color, it varies in the same way as rosin. Compounded with rubber, it is used in a metal to metal cement.

*Metal to Metal Cement*⁸

Rubber	2 oz.
Ester Gum	2 oz.
Gasoline	2 oz.
Acetone	10 oz.

DISSOLVE IN THE COLD

When rosin reacts with methyl or ethyl alcohol, liquid resins are obtained. They are called methyl abietate and ethyl abietate and are useful as plasticizers. We have seen one example of their application in the formula for an electrical sealing compound, previously given.

⁷ Same as 5, p. 41.

⁸ British Patent 439,657.

Rosin and its derivatives are not stable in light and air. Since these changes occur much faster when powdered, the rosin should be stored in lump form until it is to be used. The instability of rosin can be eliminated by transforming it chemically into a closely related substance called hydrogenated rosin. This new compound can be combined with glycerin, ethyl alcohol and methyl alcohol to produce resins which, in physical characteristics, resemble the corresponding products made from rosin, but differ from the latter in that they are not discolored by exposure to light.

CHAPTER XVI

GUMS AND RESINS

NATURAL AND SYNTHETIC

ORIGINALLY, the name gum was applied to water soluble products and the term resin implied a water insoluble material. This distinction has disappeared and the two terms are synonymous. Rosin and shellac belong to the family of natural resins, although they are frequently considered by themselves, probably due to their great commercial importance. We considered rosin in some detail in Chapter III but shall include shellac in our discussion of the other natural gums.

Shellac, unlike the other natural resins, is not an exudation produced by a tree or a plant, but is a resinous excretion of a parasitic insect that infests certain varieties of fig trees in India. The twigs containing the excretion are broken off and crushed to separate the wood. The residue is washed with warm water to remove the water soluble coloring matter. The material is dried at this stage and is known as seed lac. When the seed lac is dry, it is melted, generally after the addition of a little rosin to lower its melting point, and strained through fine mesh cloth.

The resin passes through the cloth and is caught in warm water. While still warm and plastic, the shellac is drawn into thin sheets.

Shellac does not have a definite melting point but begins to soften at about 40°C. It is soluble in ethyl and methyl alcohol but gives a milky solution because shellac contains about 6 per cent of a characteristic wax.

Shellac is completely soluble in alkalies such as sodium and potassium carbonate and borax.

Shellac may be bleached with sodium hypochlorite but, in this connection, it is interesting to note that bleached shellac gradually becomes less soluble in alcohol on long standing or warming. For some purposes, the bleached shellac is preferred because it has greater hardness and elasticity than the other alcohol soluble gums.

In many cases shellac is compounded with other natural resins to impart hardness and with plasticizers, such as castor oil, to improve flexibility. Such cements are used to unite impervious surfaces but they are neither resistant to heat nor the action of many solvents.

*Metal to Metal Cement*¹

Shellac (Bleached)	100 gm.
Sandarac Gum	40 gm.
Castor Oil	15 gm.
Alcohol (Denatured)	430 gm.

*Porcelain and China Cement*²

Shellac (Bleached)	50 lb.
Mastic Gum	35 lb.
Venice Turpentine	10 lb.
Zinc Oxide	5 lb.

Melt the resins on a water bath and add the pigment slowly with stirring. The Venice turpentine is finally stirred in. This cement is used as a sealing wax and the fractured parts are pressed together while hot.

¹ H. Bennett Chemical Formulary, Vol. II, p. 25.

² Same as 2, p. 19.

The natural resins originate in the Congo area of Africa, Malaya, the Philippine Islands, Netherlands East Indies and New Zealand. In one classification these resins are separated into two large groups, the alcohol or solvent soluble and the oil soluble resins. The alcohol soluble resins are soluble in solvents without previous treatment and are soft. The oil soluble resins must be heated to temperatures, above their melting points, to make them oil soluble and are hard. According to a second classification, the resins are placed into three major groups, the damars, the copals and a miscellaneous group of resins. In the first group are found Batavia and Singapore damar which are both oil and alcohol soluble, and the semi-fossil East Indian resins such as batu, black and pale East India, Singapore and Macassar resins. These too are oil and alcohol soluble. In the second group, the copals are found: loba and Pontianak, which are all alcohol soluble and are named in the order of increasing hardness. The bold, which refers to large clean pieces, are the hardest of this group and are oil soluble. The second group also includes the hard Congo and kauri gums, both of which are oil soluble. In the third miscellaneous group, we have the red gums, elemi, mastic and sandarac, all of which are alcohol soluble.

It is impossible to sharply define the properties of the natural resins since the transition in characteristics from resin to resin is gradual and not abrupt. Even different lots of the same resin vary from each other somewhat in their physical properties.

It is customary to designate lots by the size of the pieces. Nubs, chips, seeds and dust are named in the order of decreasing size. With decreasing size, the gum usually carries with it increasing amounts of foreign matter. The term "scraped" refers to an operation which removes surface coatings, dirt, oxidized resin, etc.

Damar resin is an exudation from a species of trees which

appears when the tree is either wounded or tapped. It is soluble in benzene and petroleum solvents, esters, chloroform and carbon bisulfide, but only partially soluble in ethyl alcohol. Damar contains an insoluble wax which must be removed before it can be used in lacquers. Damar is harder than rosin but can be scratched with the finger nail. It softens and becomes tacky at body temperature.

The copals are resins used in varnish manufacture. The softer varieties are tapped from trees while the harder and most prized grades are fossil types, which are dug from the earth. The hardness of Manila copal varies with the age of the tapping. The gum collected from a fresh incision is softer than that obtained one or two months later.

The kauri resins are found as newly formed and fossil products. The newly formed resins is obtained from living trees whereas the more important fossil kauri is darker in color and is dug from the earth.

The elemi resins are very soft resins and are white or colorless. They are soluble in alcohol, ether and chloroform.

Mastic gum is obtained on the island of Chios, off the Greek mainland. It is soluble in alcohol and turpentine.

Sandarac gum is obtained from certain coniferous trees both in Africa and Australia. It is a plastic gum but has rather high softening and melting points. It is soluble in acetone, alcohol, amyl acetate, and butyl alcohol, but is only partially soluble in benzene and turpentine.

As in the case of shellac, the natural resins are generally not used alone but are compounded with other materials to form adhesives. In some cases, solvents are used. The choice of solvents is important, not only because the solubility of the resins varies with the solvents or combination of solvents, but also because the viscosity of a gum solution changes with the solvent.

The art of compounding is learned by long practice, but the formulas given in this text can act as a guide.

Adhesive Tape Composition ³

Copal Resin	80 gm.
Castor Oil	20 gm.
Melt together and stir until uniform.	

Linoleum Cement ⁴

Batu Resin (Scraped)	30 lb.
Petroleum Thinner	30 lb.
Fuller's Earth	To suit.

The solubility of the resins in petroleum solvents varies widely depending upon its source, distillation range, etc. The proper petroleum product of high solvency must be chosen by actual test. The Batu resin is dissolved in the thinner and, enough Fuller's earth is stirred in to give a paste of the desired consistency.

Waterproof Adhesive ⁵

Gum Elemi	49 lb.
Castor Oil	1 lb.

Melt at as low a temperature as possible and stir until homogeneous. It is a very light colored, stiff, and tacky paste. With increasing amounts of castor oil, the adhesive

³ British Patent No. 481,593.

⁴ Same as 1, p. 20.

⁵ Same as 1, p. 28.

becomes softer and less tacky. By the addition of damar resin the adhesive is made harder.

*Adhesive for Glass*⁶

Rosin	7.5 lb.
Congo Resin (Heat Processed)	2.5 lb.
Dry Color	0.5 lb.

Melt the rosin and Congo resin together and stir in the color. This adhesive must be used hot.

*Envelope Adhesive*⁷

Sandarac Resin	10 gm.
Copal Resin	3 gm.
Shellac (Orange)	4 gm.
Rosin	3 gm.
Venice Turpentine	2 gm.
Turpentine	40 cc.
Alcohol	40 cc.

*Gasket Cement*⁵

Batu Scraped	50.0 lb.
Toluol	4.7 lb.
Mineral Spirits	42.5 lb.

The Batu resin is dissolved in the toluol and half the mineral spirits. When the resin is in solution, the rest of the mineral spirits is added.

⁶ Same as 1, p. 30.

⁷ Same as 1, p. 17.

*Cement for Floor Covering**(Formula 1)⁴*

Manila Resin DBB	30 lb.
Alcohol, Denatured	15 lb.
Union Solvent #8	40 lb.
Fuller's Earth	

(Formula 2)⁸

Linseed Oil (Oxidized, Alcohol Soluble) .	27-35 gm.
Manila Resin	6-10 gm.
Bentonite	35-40 gm.
Alcohol (Denatured)	25 gm.

The linseed oil and resins are dissolved in the alcohol and the bentonite is stirred in. The letters D B B after manila resin indicate degree of hardness and are part of a conventional system of nomenclature. WS, MA and MB designate soft Manila copals.

Tin Can Sealer⁹

Manila Resin WS	150 lb.
Elemi Resin	5 lb.
Ether	100 lb.
Alcohol (Denatured)	55 lb.

⁸ U. S. Patent No. 2,064,139.

⁹ Same as 1, p. 26.

CHAPTER XVII

ADHESIVES DERIVED FROM SYNTHETIC MATERIALS

ONE of the most outstanding achievements of industrial chemistry, in recent years, has been the production of various types of resins and plastics. Many of the resins used in adhesives were developed several years ago but some of the most complicated and valuable products are of rather recent origin.

Coal tar naphtha, boiling approximately between 150–200°C. is the source of two interesting chemical compounds called coumarone and indene. By rather complicated chemical treatment, these raw materials are converted into a series of valuable resins.

A sugar derivative, sucrose octa-acetate, has been proposed as a thermoplastic and as a solution type of adhesive. Although it is practically insoluble in water, it is soluble in acetone, toluene and alcohol.

Glyceryl phthalate is recommended in the manufacture of thermosetting cements to replace shellac in order to impart better thermoplastic properties to the cement.

Glyceryl phthalates are modified with both drying and non-drying vegetable oils to produce an important class of resins known as alkyd resins. Some of these are sticky resins useful as adhesives. Depending upon their composition some grades are soluble in toluene and lacquer solvents while others dissolve in petroleum solvents.

In plywood manufacture, four different types of adhesives are considered, vegetable glue, animal glue, casein glue and synthetic resins. The first three types, we have already studied. The synthetic resins are the strongest

adhesives ever developed for the woodworking trade. For this work the "Bakelite" type of resins are used, or in chemical terminology, the phenol-formaldehyde, urea-formaldehyde, acrylic and other thermosetting resins. These resins can be blended with animal glues to produce strong, water-proof adhesives. In this instance, it is necessary to break down the glue in order to compound it with the Bakelite resin.

Synthetic Resin Adhesives

Formaldehyde (40%)	500 lbs.
Cresylic Acid (Dark)	1000 lbs.
Bleaching Powder	20 lbs.
Hide Glue (Ground)	1200 lbs.
Sodium Bicarbonate	24 lbs.
Water	2000 lbs.

Run the formaldehyde into the cresylic acid. Add the bleaching powder gradually and maintain the temperature at 90°C. for 30 minutes. Let the resin stand one hour.

Dissolve the hide glue and sodium bicarbonate in the water and heat the solution in an autoclave at 130°C. for 2.5-3 hours.

Numerous modifications of phenol formaldehyde resins have been developed in which various compounds related to phenol (carbolic acid) are used. Related substances have been substituted for formaldehyde. Very complicated reactions are involved in these processes but suffice to say that a large number of valuable resins, suitable as adhesives, have been developed. These need not be blended with any other adhesive material as in the example cited last.

A blend of phenol-formaldehyde resin, coumarone resin

and Portland cement has been proposed as a linoleum cement.

The urea formaldehyde resins constitute the second group of adhesive resins important in plywood manufacture. Urea and formaldehyde react to form first a water soluble substance, called dimethylolurea, which can be prepared in various concentrations and viscosities. This substance can be insolubilized by further treatment.

Dimethylolurea has been modified with casein and used as a glue for plywood by setting in a press at 100°C.

Plywood Glue

Casein	500 lbs.
Dimethylolurea	500 lbs.

Thiourea is much more expensive than urea but it is used to improve the transparency of urea formaldehyde resins.

Transparent Resin Adhesive

Urea	200 lbs.
Thiourea	52 lbs.
Trioxymethylene	240 lbs.
Sodium Acetate	6 lbs.
Formamide	20 lbs.

Heat the intimate mixture to 140°C. for 20 minutes. The melt becomes viscous and on cooking solidifies into a hard, white mass which may be powdered and used as a thermoplastic adhesive.

Trioxymethylene is a solid modification of formaldehyde. Formamide is a slightly alkaline substance which acts as a catalyst in the reaction.

The phenol resins are stronger than the urea resins and much more resistant to heat and water, and bacterial decomposition than the latter. Consequently, resin adhesives have made possible the use of plywoods for outdoor purposes. Such plywoods are known as plastic plywoods.

Like plywood, safety glass has a laminated structure. The outer surfaces are plate glass, and between them there generally is a sheet of transparent, plastic material. These layers are held together by a strong, flexible plastic adhesive that must adhere strongly to glass and withstand rapid and wide variations in temperature and moisture. Of course, it must be absolutely transparent and must not be affected by sunlight. None of the adhesives we have so far encountered meet these specifications. Not many years ago synthetic chemistry supplied the required material in a substance called polyvinyl acetate.

Polyvinyl acetate is sold as a white, tasteless and odorless powder. It is thermoplastic and becomes very tacky at 93°C. It is soluble in acetone, alcohol and butyl acetate. The resin is unaffected by dilute acids or alkalies. It may be blended, in solution, with other materials to produce adhesives for paper, metal, plastics, glass, textile, leather, etc.

Polyvinyl acetate has been proposed for binding abrasives to steel discs. It is also used for the manufacture of compound sheets of thin foils of cellulose derivatives.

Combined with ethyl acetanilid, and cellulose acetate or ethyl cellulose, polyvinyl acetate is proposed as a plastic adhesive.

As a liquid adhesive it is combined with a cellulose derivative to impart toughness.

Light Polyvinyl Adhesive

Vinyl Acetate Resin	40 lbs.
Cellulose Acetate or Nitrate	4-12 lbs.
Volatile Solvent	60 lbs.

In another form of liquid adhesive, polyvinyl acetate is dissolved in methyl alcohol and plasticized with isobutyl-phthalate.

Polyvinyl acetate is not considered strong enough to be the only filler for the sandwich of glass which makes up safety glass. A sheet of a cellulose derivative is generally used to impart strength to the filler. Cellulose nitrate may be used, but it tends to turn yellow on exposure to sunlight. Several ways have been found to overcome this difficulty. A sheet of cellulose acetate may be used instead of the nitrate. It has been observed that the defect can be partially remedied by using a mixture of cellulose nitrate and vinyl resin.

The use of a reinforcement of cellulose derivative may be avoided by plasticizing the polyvinyl acetate with 5-25% camphor and dibutyl phthalate.

Celluloid may be glued to glass with an adhesive composed of polyvinyl acetate, formaldehyde-toluene-sulfonamide and dibutyl phthalate.

There is another colorless, transparent resin which is said to find application as an adhesive for safety glass. This resin is a derivative of acrylic or methacrylic acid. One cement proposed is obtained from a mixture of methyl acrylate and ethyl methacrylate. The methacrylate resins may be used for glueing.

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CHAPTER XVIII

WAX ADHESIVES

NATURAL waxes are animal, vegetable and mineral in origin. Their properties vary widely, depending upon their source. The animal and vegetable waxes are closely related to fats but differ from them in that they display little greasiness at room temperature. Most of the natural and synthetic waxes melt well below 100°C. and are generally applied in molten form.

A number of different natural and synthetic waxes, generally compounded with plasticizers, find application as cements and sealing compounds.

Certain of the solid animal fats are used as inexpensive substitutes for waxes. The most important products of this group are tallow and lard. Tallow, the solid fat of oxen and sheep melts between 45 and 55°C. Lard, the solid fat of hogs, melts between 30 and 49°C.

There are a number of synthetic solid fats which have higher melting points and greater hardness than the natural fats. They are what the chemist calls hydrogenated vegetable oils and are derivatives of cottonseed oil, soy bean oil, castor oil and fatty oils obtained from marine mammals.

Chemically, the true waxes are distinguished from the fats in that both animal and vegetable fats are chemical combinations with glycerin whereas the synthetic waxes usually contain no glycerin, but higher alcohols.

Beeswax is obtained from the honeycomb of bees. The comb is melted, the impurities are strained off and the wax is run into molds. The wax is bleached either by exposure to sunlight or by treatment with oxidizing agents such as

nitric acid, chromic acid or hydrogen peroxide. Yellow beeswax smells of honey while the bleached product is odorless. Being rather expensive and hard, beeswax may be compounded with animal fats to produce a wax for sealing or calking casks.

*Calking Wax*¹

Beeswax (Yellow)	20 lb.
Tallow (Beef)	25 lb.
Lard	40 lb.

For technical purposes such as the above, one may substitute B.Z. Wax A or other synthetic waxes for beeswax.

A product for calking boats has been produced from beeswax.

*Boat Calking Wax*¹

Beeswax	4 lb.
White Lead Paste (in Linseed Oil) ...	5 lb.

Wax adhesives are frequently used to fill in holes, joints, splits, cracks or other flaws in furniture or other wooden articles.

*Wood Filler*¹

Beeswax	10 lb.
Rosin	10 lb.
Sawdust	to suit

¹ Fischer, E. J., *Wachse, Wachsähnliche Stoffe und Technische Wachsgemenge*, p. 75, Verlag von Theodor Steinkopff, (Dresden und Leipzig) (1934).

Melt the beeswax and rosin and stir in enough sawdust so that a hard mass is obtained on cooling.

Beeswax may also be used in an adhesive for glass to metal.

*Adhesive Glass to Metal*¹

Beeswax (Bleached)	2 lb.
Rosin	4 lb.
Venetian Turpentine	1 lb.
English Red	4 lb.

Melt the wax and rosin and stir in the English Red.

Wool grease is the natural grease which encrusts raw sheep's wool. Sometimes it is extracted by solvents but usually by washing the wool with soap and soda ash. The wool fat is emulsified and is separated by acidifying the emulsion with sulfuric acid. Purified wool grease is called lanolin. Chemically it is more like a wax than a fat as it contains no glycerin.

Japan wax is derived from the berries of three species of *Rhus* that grow in Japan. The berries are ground to a meal, heated in a hemp bag, with steam, and pressed. The residue is heated and pressed a second time. The wax is further purified by skimming the dirt off the molten wax and straining it through cloth. The molten wax is pressed through woolen bags into water and forms fine grains. The fine wax particles are separated from the water and bleached in the sun for thirty days. The commercial wax is hard, and pale yellow in color. Its melting point varies from 48 to 55°C. Japan wax is insoluble in alcohol but soluble in benzene and petroleum ether.

Mixtures containing Japan wax and wool fat are used to repair bad scrapes or cuts in furniture.

*Wax Furniture Filler*¹

Japan Wax	30 lb.
Paraffin Wax	10 lb.
Wool Fat (Neutral)	10 lb.
Rosin	40 lb.

The waxes are simply melted together.

Carnauba wax is exuded from the leaves of a Brazilian palm. Its melting point, 84°C., is higher than that of the other natural waxes. It is also prized because of its great strength, hardness and gloss.

Waxes for sealing bottles must be hard and strong. For this reason carnauba wax is an important component of sealing cements.

*Bottle Sealing Wax*²

Carnauba Wax	30 kg.
Beeswax	20 kg.
Paraffin Wax (m.p. 50°–52°C.)	20 kg.
Whiting	4 kg.
Barytes	10 kg.
Chrome Orange	16 kg.

Melt the waxes together and stir in the pigments.

Carnauba wax is also used as a component to fill in flaws in cast iron castings.

² Bennett, H., Chemical Formulary, Vol. V, p. 33, Chemical Publishing Co. (1940).

*Filler for Cast Iron*²

Paraffin Wax	20 lb.
Carnauba Wax	10 lb.
Rosin	20 lb.
Iron Borings (Fine)	20 lb.
Graphite	10 lb.

The waxes and rosin are melted and the iron borings and graphite are stirred in.

Montan wax is a mineral wax. It is a bituminous substance which can be extracted from lignites by various solvents. The refined substance is hard and odorless. It melts between 76° and 90°C. In commerce it appears as a black or tan, high melting, candle-like material. Chemically, it is not a paraffin but is composed largely of montanic acid and esters.

Ceresin is another important mineral wax. It is derived from ozokerite, a natural paraffin found in Galicia and Baku. Ceresin is an odorless brilliant white wax which is transparent in thin layers. It is harder than paraffin wax, does not "sweat out" as the latter sometimes does, and usually has a crystalline structure. It is unaffected by acids and alkalies. Its melting point is 75–80°C. It may be used as a substitute for beeswax in some cases.

Paraffin wax is a constituent of the high boiling residue obtained by the distillation of certain crude oils. There are a number of grades on the market which are based on melting point and crystal structure. Paraffin wax is chemically inert and is unaffected by acids and alkalies.

Microcrystalline waxes, gotten from petroleum have a higher melting point and adhesiveness than paraffin wax.

The mineral waxes which we have just described are compounded in various ways to serve numerous useful

purposes. We can cite only a limited number of examples.

Wax mixtures are used to fill nail holes and hide defects in leather products such as shoes.

Leather Filler ²

(Formula 1)

Paraffin	70 gm.
Rosin	30 gm.
Leather Color or Lampblack	

Add enough coloring matter to the molten wax and rosin to obtain the desired color.

(Formula 2)

Montan Wax (Crude)	32 lb.
Paraffin Wax (Soft)	19 lb.
Rosin	24 lb.
Rosin Oil	24 lb.
Boneblack	1 lb.

Wax cements are used to repair cracks or fractures in stoneware.

Stoneware Cement

Paraffin Wax	30 lb.
Rosin	20 lb.
White Sand	25 lb.
Emery (Grainy)	15 lb.
Tripoli	15 lb.

This cement is applied hot.

*Wax Wood Filler*¹

Paraffin Wax	50 lb.
Montan Wax	10 lb.
Rosin	40 lb.

The wax and rosin mixture is colored either with mineral colors or coal tar dyes.

An especially flexible bottle sealing wax which is insoluble in alcohol is prepared from a mixture of waxes.

*Flexible Bottle Sealing Wax*²

Montan Wax	8 kg.
Japan Wax	20 kg.
Paraffin Wax	52 kg.
Lithopone	20 kg.

The lithopone is stirred into the molten waxes.

Tree surgery and horticulture are limited, but important fields for the application of wax cements. They are applied when limbs of trees are cut off and in the grafting of fruit trees. The waxes prevent loss of sap, infection, insect attack and reduce scarring. Generally the mixture contains beeswax, ceresin, rosin oil and fat. The products may be placed in two groups. The first group is fluid or salve-like in the cold, whereas the other becomes hard on cooling.

*Grafting Wax Salve*¹

Rosin Oil	5 lb.
Rosin	80 lb.
Petrolatum (Yellow)	15 lb.

*Grafting Wax*¹

Rosin	50 lb.
Wool Fat	20 lb.
Ceresin (58–60°C.)	15 lb.
Beeswax	5 lb.
Rosin Oil	10 lb.

There are many proprietary waxes sold. Very little information has been published about them so that we can only mention a few that may be of value in adhesives, special micro-crystalline paraffin waxes, Bardnsdall Special Waxes; Acrawax, B. Z. Wax A, Flexo Wax C, and Opal Wax.

CHAPTER XIX

PUTTIES

PUTTIES are a group of adhesives used to form a hardening nonflexible bond between hard surfaces. Some representative examples, made according to the materials to be joined, are listed below.

To join:

Metal and Stone

Stir cold sodium silicate (38° Bé) with whiting to a thick dough; use immediately.

Brass and Marble

Sodium Oxid	7.5
Water	40.0
Rosin	22.5

Boil and mix with 35 gypsum. Use when warm; hardens after 40 minutes.

*Metal and China **

Guttapercha	2
Beeswax	1
Sealing wax	3

Fuse the ingredients and warm the joints before applying the putty.

* China refers to any type of ceramic.

*Metal and Glass**Metal and Wood**Metal and China*

Shellac	1
Pumice (Powdered)	1

Fuse, stir and use while hot.

*Metal and Horn ***

Guttapercha	6
Coal Tar pitch	4

Fuse, stir and use while hot.

*Rubber and Glass**Rubber and Stone**Rubber and Metal*

a) Guttapercha	10
Carbon disulfide	40
Dissolve while cold.	
b) Shellac	14
Venetian turpentine . . .	1
Alcohol	35

Dissolve b and mix with a.

Metal and Linoleum

Coumarone	20
Coal Tar Pitch	3

Fuse and mix with 2 naphtha solvent, use while hot.

** Horn refers to shell, ivory, horn, bones.

Metal and Celluloid

Rosin	33
Camphor	2
Alcohol	65

Brush joints with the above solution and press them together.

Stone and Stone

Kieselguhr	1
Litharge	3
Slaked Lime	2

Mix and stir with linseed oil, varnish to tough dough.

Stone and Horn

Shellac	5
Guttapercha	4

Fuse and use like sealing wax.

Stone and Hard Rubber

Guttapercha	2
Rosin	5

Fuse and mix with 2 pine tar.

China and China

Shellac	15
Mastic	5
Venetian turpentine	1
Alcohol	60

Dissolve with gentle heat.

Glass and Glass

Rubber	1
Mastic	16
Chloroform	70
Dissolve by shaking.	

Glass and Wood

Whiting	75
Linseed oil	9
Knead to a tough dough.	

Marine Glue

Pitch	3
Shellac	2
Crude Rubber	1
Melt and stir.	

***Putty for Knife Handles* (and other parts which are subjected to heavy strain) :**

Mix powdered litharge with syrupy glycerin and apply.
This compound hardens very rapidly.

REFERENCE

Hopkins: Scientific American Cyclopedia of Formulas; Scientific American.

TRADE MARKED PRODUCTS

"Cellite"	(6)
"Clovel"	(4)
"Dowicide A"	(2)
"Gardinol"	(3)

"Moldex"	(4)
"Protoflex"	(4)
"Protovac"	(1)
"RH 349"	(3)
"Santomerse"	(7)
"Staybelite"	(5)
"Sulfatate"	(4)
"Wetanol"	(4)
"Yumidol"	(4)

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- (1) Casein Corp. of America, New York, N. Y.
- (2) Dow Chemical Co., Midland, Mich.
- (3) E. I. du Pont de Nemours & Co., Wilmington, Del.
- (4) Glyco Products Co., Inc., Brooklyn, N. Y.
- (5) Hercules Powder Co., Wilmington, Del.
- (6) Johns Manville Co., New York, N. Y.
- (7) Monsanto Chemical Co., St. Louis, Mo.

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